By heating benzoic acid, NaCl, and $K_2S_2O_7$ at 200° (Beketoff, *A.* 109, 256).—6. By the action of $COCl_2$ on benzene in presence of Al_2Cl_6 (Friedel, Crafts, a. Ador, *B.* 10, 1855).—7. From benzoic acid or benzoates and S_2Cl_2 (Carius, *A.* 106, 300).—8. By heating benzoic acid with $ZnCl_2$ and adding benzotrichloride (*D. P. J.* 239, 157). $C_6H_5CCl_3 + C_6H_5.CO_2H = 2C_6H_5.COCl + HCl$.

Properties.—Colourless pungent oil. Decomposed into HCl and benzoic acid slowly by cold, quickly by hot, water. Alcohol reacts vigorously, forming benzoic ether and HCl. Ether and CS_2 dissolve it without decomposition.

Reactions.—1. Aqueous KOH gives KOBz and KCl.—2. Dry BaO at 150° forms Bz_2O (Gal, *A.* 128, 127).—3. Dry NH_3 or *ammonium carbonate* forms benzamide; other bases act similarly.—4. *Sodium* has no action in the cold, but in presence of ether at 100°, 'dibenzoyl' [140°] is slowly formed (Briegel, *Bl.* [2] 5, 278). 5. *Hydride of Copper* forms Cu_2Cl_2 and benzoic aldehyde (Chiozza, *A.* 85, 232).—6. KI forms BzI.—7. $HgCy_2$ forms BzCy.—8. KSCN forms benzonitrile, CO_2, and CS_2 (Limpricht, *A.* 99, 117).—9. $Pb(SCN)_2$ forms BzSCN.—10. KNCO forms benzonitrile (Schiff, *A.* 101, 93) and cyaphenine (Cloez, *Bl.* 1859, 100).—11. NaOBz gives Bz_2O (Gerhardt).—12. *Sodium formate* forms CO, NaCl, and benzoic acid.—13. Potassium oxalate forms Bz_2O, KCl, CO, and CO_2.—14. By the dry nitrates of Pb, Ag, Hg, or Cu, it is converted into benzoic anhydride, with formation of the chloride of the metal, N_2O_4, and oxygen (Lachowicz, *B.* 18, 2990).—15. Conc. H_2SO_4 forms, apparently, $Bz.SO_4H$, which on heating becomes benzene-sulphonic acid (Oppenheim, *Z.* [2] 7, 21).—16. PCl_5 at 200° gives $C_6H_5.CCl_3$, $C_6H_4Cl.CCl_3$, $C_6H_3Cl_2.CCl_3$ and at a higher temperature CCl_4 and chlorinated benzenes (Schischkoff a. Rösing, *J.* 1858, 279; Limpricht, *A.* 134, 55; Claus a. Hoch, *B.* 19, 1194).—17. KHS forms BzSH.—18. BaO_2 gives Bz_2O_2.—19. *Sodium amalgam* in acid solution forms benzoic aldehyde and benzyl alcohol (Lippmann, *A.* 137, 252).—20. KNH_2 forms benzamide and dibenzamide (Baumert a. Landolt, *A.* 111, 1).—21. *Succinic ether* at 200° gives succinic anhydride, EtOBz, and EtCl (Kraut, *A.* 137, 254).

Combination.—$TiCl_4BzCl$. [65°]. Yellow crystals (Bertrand, *Bl.* [2] 34, 631).

BENZOYL-CHLORO-TOLUIDE *v.* CHLORO-TOLUIDINE.

BENZOYL-CHOLIC ACID *v.* CHOLIC ACID.

BENZOYL-CROTONIC ACID $C_{11}H_{10}O_3$ *i.e.* $C_6H_5.CO.C(CH_3):CH.CO_2H$. [113°]. Long pointed crystals. Prepared by the action of Al_2Cl_6 on a mixture of benzene and citraconic anhydride. By alkalis it is resolved into phenyl ethyl ketone and glyoxylic acid (Pechmann, *B.* 15, 891).

BENZOYL-CUMIDIC ACID *v.* PHENYL-XYLYL-KETONE DI-CARBOXYLIC ACID.

BENZOYL CUMIDINE *v.* CUMIDINE.

BENZOYL-CYANACETIC ETHER *v.* CYANO-BENZOYL-ACETIC ETHER.

BENZOYL CYANIDE $C_6H_5.CO.CN$. [33°]. (208°). Formed by distilling BzCl with $HgCy_2$ or AgCy (Liebig a. Wöhler, *A.* 3, 267; H. Strecker, *A.* 90, 62; Hübner a. Buchka, *B.* 10, 480; Kolbe, *A.* 90, 63; 98, 347). Formed also by mixing isonitroso-acetophenone $C_6H_5.CO.CH:NOH$ with AcCl in the cold, and then distilling the mixture. The isonitroso-acetophenone need not be separately prepared, but amyl nitrite (1 mol.) can be allowed to drop slowly into a warm mixture of acetophenone (1 mol.) and acetyl chloride (3 mols.), and the product distilled; yield: 65–70 p.c. of the theoretical (Claisen a. Manasse, *B.* 20, 2196). Pungent crystalline mass. Decomposed slowly by water, more readily by KOHAq into HOBz and HCN. Fuming HCl forms $C_6H_5.CO.CO.NH_2$, whence phenyl-glyoxylic acid. Zinc and HCl reduce it to benzoic aldehyde. NH_3 gives benzamide and NH_4CN. *Aniline* gives benzanilide. PCl_5 appears to form $C_6H_5.CCl_2.CN$ (224°) (Claisen, *B.* 12, 626). $ZnEt_2$, diluted with other forms 3 p.c. of 'benzcyanidine' $C_{24}H_{19}NO_2$, [121°], needles (from alcohol); another product (200°–220°), either contains phenyl ethyl ketone or yields that body on oxidation (Frankland a. Louis, *C. J.* 37, 742).

BENZOYL CYANIDINE *v.* BENZOYL CYANIDE.

BENZOYL CYANURATE *v.* CYANURIC ACID.

BENZOYL - CYMENE - SULPHAMIDE *v.* CYMENE SULPHONIC ACID.

BENZOYL-CYMENOL *v.* CYMENOL.

BENZOYL CYMIDIDE *v.* CYMIDINE.

BENZOYL DESOXALIC ACID *v.* DESOXALIC ACID.

BENZOYL-ISODURENE *v.* PHENYL TETRA-METHYL-PHENYL KETONE.

o-**TRI-BENZOYLENE-BENZENE** $C_{27}H_{12}O_3$ *i.e.* $C_6(C_6H_4CO)_3$. [above 360°]. Formed together with methylene-phthalyl by heating phthalic anhydride with malonic ether and sodium acetate, or by the action of H_2SO_4 on phthalyl-acetic acid (Gabriel a. Michael, *B.* 10, 1557; 11, 1007, 1679; 14, 925). Yellow crystals. Soluble in nitrobenzene, nearly insoluble in other solvents. Potash-fusion converts it into phenenyl-tri-benzoic acid $C_6H_3(C_6H_4CO_2H)_3$ [261°].

DI - BENZOYL - ETHANE *v.* DI - PHENYL-ETHYLENE-DI-KETONE.

BENZOYL - ETHYL - ACETIC ACID *v.* BENZOYL ACETIC ACID.

BENZOYL - ETHYL - ANILINE *v.* ETHYL-ANILINE.

BENZOYL - ETHYL - BENZENE *v.* PHENYL ETHYL-PHENYL KETONE.

BENZOYL-ETHYL-*o*-CARBOXYLIC ACID *v.* PHENYL ETHYL KETONE *o*-CARBOXYLIC ACID.

BENZOYL-FORMIC ACID *v.* PHENYL-GLYOXYLIC ACID.

BENZOYL FLUORIDE $C_6H_5.CO.F$. (162°). From HKF_2 and BzCl (Borodin, *A.* 126, 60). Pungent liquid; attacks glass. Decomposed by water into HF and HOBz.

DI-BENZOYL-FUMARIC ETHER $CO_2Et.CBz:CBz.CO_2Et$. Formed by the action of iodine dissolved in ether upon the di-sodium compound of di-benzoyl-succinate, $CO_2Et.CBzNa.CBzNa.CO_2Et$ (Perkin, *C. J.* 47, 262).

BENZOYL-GALLIC ACID *v.* GALLIC ACID.

BENZOYL-GLYCOCOLL *v.* HIPPURIC ACID.

BENZOYL-GLYCOLLIC ACID *v.* GLYCOLLIC ACID.

α-**BENZOYL - ISO - HEXOIC ACID** *v.* *Iso-butyl*-BENZOYL-ACETIC ACID.

BENZOYL HYDRIDE v. BENZOIC ALDEHYDE.

DI-BENZOYL-IMIDE v. p. 475.

DI-BENZOYL-INDIGO v. INDIGO.

BENZOYL IODANILINE v. IODO-ANILINE.

BENZOYL IODIDE $C_6H_5.CO.I$. Easily-fusible crystalline mass obtained by heating BzCl with KI (Liebig a. Wöhler, *A.* 3, 266).

BENZOYL-ISATIN v. ISATIN.

BENZOYL-ISETHIONIC ACID v. ISETHIONIC ACID.

BENZOYL-LACTIC ACID v. LACTIC ACID.

BENZOYL-LEUCINE v. LEUCINE.

TRI-BENZOYL-MELAMINE v. MELAMINE.

BENZOYL-TRIMELLITIC ACID. *Benzophenone tricarboxylic acid* $C_{16}H_{10}O_7$ *i.e.* $C_6H_5.CO.C_6H_2(CO_2H)_3$ [5:1:2:4]. From phenyl ψ-cumyl ketone by oxidation with dilute HNO_3 or $KMnO_4$ (Elbs, *J. pr.* [2] 35, 494). **Salts.**—$BaHA'''$.

BENZOYL-MESIDIDE v. MESIDINE.

BENZOYL-MESITYLENE v. PHENYL TRI-METHYL-PHENYL KETONE.

Dibenzoyl-mesitylene v. DI-PHENYL TRI-METHYL-PHENYLENE DIKETONE.

Tri-benzoyl-mesitylene $C_{30}H_{24}O_3$ *i.e.* $(C_6H_5.CO)_3C_6Me_3$. *Tri-phenyl tri-methyl-phenenyl tri-ketone.* [216°]. Formed by heating benzoyl mesitylene or di-benzoyl-mesitylene with BzCl and Al_2Cl_6 at 198°. Crystals (from alcohol), v. sl. sol. cold alcohol, v. sol. a mixture of chloroform and acetone. When BzCl acts on mesitylene in presence of Al_2Cl_6 below 118° only benzoyl-mesitylene is formed; at 150° di-benzoyl-mesitylene is the chief product (Louise, *C. R.* 98, 1440; *A. Ch.* [6] 6, 237).

o-BENZOYL-MESITYLENIC ACID $C_{16}H_{14}O_3$ *i.e.* $C_6H_5.CO.C_6H_2Me_2COOH$. *Phenyl xylyl ketone carboxylic acid.* [185°]. Prepared in the same way as the *p*- acid (*v. infra*) (Louise, *Bl.* [2] 44, 418). Colourless crystals, insol. cold water, sl. sol. boiling water, sol. $CHCl_3$, acetone, ether, and benzene. Its salts do not crystallise well.—AgA'. CuA'_2.

p-Benzoyl-mesitylenic acid $C_{16}H_{14}O_3$. [160°]. Prepared by oxidising phenyl tri-methyl-phenyl ketone (benzoyl-mesitylene) (Louise, *Bl.* [2] 44, 418; *A. Ch.* [6] 6, 218). Nacreous scales, very sol. ether, $CHCl_3$, acetone, &c., sol. boiling water.

Salts.—$A'NH_4$: small brilliant crystals.—A'Ag: white pp. sol. boiling water. A'_2Ba 2aq: long needles. A'_2Ca: long white filaments.—A'_2Mg 6aq: crystals, sol. hot water.—SrA'_2.

BENZOYL-METHANE v. ACETOPHENONE.

Di-benzoyl-methane v. DI-PHENYL METHYLENE DIKETONE.

Tri-benzoyl-methane $(C_6H_5.CO)_3CH$. *Methenyl tri-phenyl tri-ketone* [225°]. Formed by the action of benzoyl-chloride on sodio-di-benzoyl-methane (Baeyer a. Perkin, *B.* 16, 2135; *C. J.* 47, 240). Small needles. Sublimable. V. sl. sol. alcohol, v. sol. dilute alcoholic KOH. Converted by NaOEt and BzCl into a substance [260°-270°].

BENZOYL-METHYLAMINE v. METHYL-AMINE.

BENZOYL-METHYL-ANILINE v. METHYL-ANILINE.

BENZOYL-DIMETHYLANILINE v. DI-METHYL-AMIDO-BENZOPHENONE.

BENZOYL-TRIMETHYLENE v. PHENYL TRI-METHYLENE KETONE.

DI-β-BENZOYL-DI-METHYL-MALONIC ACID $(C_6H_5.CO.CH_2)_2C(CO_2H)_2$. *Di-phenacyl-malonic acid.* [184°]. Formed by saponification of its ether, which is obtained by the action of ω-bromo-aceto-phenone upon sodio-malonic ether. Large colourless prisms. V. sol. alcohol, ether, and acetic acid, sl. sol. water, insol. benzene and ligroïn. Reacts with phenyl-hydrazine. Evolves CO_2 on heating, giving di-benzoyl-isobutyric acid.—*$A''K_2$: white needles or plates, v. sol. water.—*$A''Ag_2$: nearly insol. white pp.

Di-ethyl ether $A''Et_2$: [119°]; large white glistening prisms or long flat needles; v. sol. water, benzene, acetic acid, and CS_2, less in alcohol, insol. ligroïn. Reacts with phenyl-hydrazine but not with hydroxylamine (Kues a. Paal, *B.* 19, 3144).

BENZOYL-METHYL-p-NITRANILINE v. *p*-NITRO-PHENYL-ω-AMIDO-ACETOPHENONE.

BENZOYL-METHYL-PHENYL-NITROS-AMINE v. PHENYL-AMIDO-ACETOPHENONE.

BENZOYL-NAPHTHALIDE v. NAPHTHYL-AMINE.

BENZOYL-NAPHTHYLAMINE-IMIDE-CHLORIDE v. ω-CHLORO-BENZYLIDINE-NAPHTHYL-AMINE.

BENZOYL-NAPHTHYL-THIO-UREA v. NAPHTHYL-THIO-UREA.

BENZOYL-NITRANILIDE v. NITRO-ANILINE.

BENZOYL-NITRITE $BzNO_2$ (?). An oil formed together with *m*-nitro-benzoic aldehyde by the action of 20 vols. of a mixture of HNO_3 (1 vol.) and H_2SO_4 (2 vols.) upon 1 vol. of benzoic aldehyde (Lippmann a. Hawliczek, *B.* 9, 1463). It is decomposed by distillation.

BENZOYL-NITRO-AMIDO-DIPHENYL v. NITRO-AMIDO-DIPHENYL.

BENZOYL-NITRO-AMIDO-PHENOL v. NITRO-AMIDO-PHENOL.

BENZOYL NITRO-ANISIDINE v. NITRO-AMIDO-PHENOL.

BENZOYL NITRO-CUMIDINE v. NITRO-CUMIDINE.

BENZOYL-NITRO-NAPHTHALIDE v. NITRO-NAPHTHYLAMINE.

BENZOYL-NITRO-DIPHENYLAMIDE v. NITRO-DIPHENYLAMINE.

BENZOYL-NITRO-TOLUENE SULPHAMIDE v. NITRO-TOLUENE SULPHONIC ACID.

BENZOYL-NITRO-TOLUIDE v. NITRO-TOLUIDINE.

BENZOYL PEROXIDE $C_{14}H_{10}O_4$ *i.e.* Bz_2O_2. [104°]. BzCl is mixed with hydrated BaO_2 and the resulting solid cake washed with water and Na_2CO_3, and crystallised from CS_2 (Brodie, *Pr.* 9, 361; 12, 655; Sperlich a. Lippmann, *Sitz. B.* 62, 613). Trimetric crystals, insol. water, v. sol. ether and benzene. Decomposed by heat, giving off CO_2 with slight explosion. Boiling KOHAq forms O and KOBz. Benzoyl peroxide acts as an oxidising agent, splitting up into Bz_2O and O: thus it oxidises *p*-toluidine to toluene-azo-toluene.

BENZOYL-PHENOL C_6H_5OBz v. PHENOL; $C_6H_5.CO.C_6H_4OH$ v. OXY-BENZOPHENONE.

BENZOYL-PHENOL SULPHONIC ACID v. PHENOL SULPHONIC ACID.

BENZOYL-PHENYL-AMINE

$C_6H_5.CO.C_6H_4NH_2$. Benzanilide (18 g.), BzCl (14g.), and $ZnCl_2$ give the *p*-benzoyl derivative [150°], together with a little of the *o*-benzoyl-

WATTS'

DICTIONARY OF CHEMISTRY

REVISED AND ENTII

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ASSISTED BY EMINENT CONTRIBUTORS

IN FOUR VOLUMES

VOL. I.

NEW IMPRESSION

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PREFACE.

TWENTY-FIVE years have passed since the publication of the first edition of *Watts' Dictionary of Chemistry* began, and it is now seven years since the second part of the last supplement was published.

Some time before his death, MR. WATTS had agreed to prepare a new edition of his Dictionary, which should give as complete an account of the present state of the science as might be found compatible with the appearance of the book in four volumes of about 750 pages each. MR. WATTS had prepared *Instructions to Contributors*, and had written sixty-three pages for the new edition, when his death—which all chemists so deeply lamented—stopped the work. It has fallen to us to take up the task dropped from worthier hands, and to endeavour to bring it to a satisfactory conclusion.

MR. WATTS' MS. is printed very much as he left it, subject only to some necessary condensation. In preparing a new edition we have found it necessary to rewrite the whole book. Our instructions were that we should give as complete and satisfactory an account of the present state of chemical science as we could, consistently with the size to which we were required to confine the book. We have been obliged, therefore, to adopt a very condensed style; the descriptions of individual bodies are given in few words, abbreviations are freely used, and formulæ are frequently employed instead of names in order to save space.

The original edition was called 'A Dictionary of Chemistry and the Allied Branches of other Sciences;' the new edition deals with chemistry only. Considerable space was devoted in the original work to processes of chemical technology; the new edition gives no special information with regard to these matters. Technical chemistry will be treated in a companion volume to be published under the editorship of Professor Thorpe. The great importance of the application of physical methods to chemical questions has made it necessary to consider these methods and the results gained by applying them. Hence in our enumeration of the properties of each element and compound we have included those physical constants which are of most importance to the chemist; and we also intend to describe the leading physical methods of investigation employed in chemistry, and to give a short account of the chief results obtained, in an article entitled *Physical Methods used in Chemistry*. This article will be divided into sections, each of which will be written by a specially qualified author.

After much consideration, it was decided to omit details regarding analytical processes. In certain cases, e.g. *Arsenic* methods of detection are given rather

fully. But the new edition is not intended for the use of the analyst in the laboratory. A sketch of the principles of analytical chemistry, and some account of the chief classes of analytical methods, are given in the article *Analysis*. We have been especially anxious to arrange the matter in a methodical manner, so as to make the task of finding the chief facts about any specified body as little laborious as possible. Cross-references are freely used.

As mere descriptions of individual bodies in strictly alphabetical order cannot suffice to give a fair notion of the present position of chemistry, we have supplemented these descriptions by short general articles on classes of elements and compounds, e.g. *Alkali Metals, Carbon Group of Elements, Oxides, Hydroxides, Hydrates*, and *Amines*. We have also devoted considerable space to articles on important theories, hypotheses, and principles. Some of these articles may be found to overlap, e.g., *Chemical Change* and *Equilibrium, Chemical*; but the great importance of the subjects treated in such articles is, in our opinion, sufficient warrant for devoting much space to their consideration, and for inviting different authors to treat parts of the same subject from different points of view.

One of the editors is responsible for the inorganic and general, and the other for the organic, chemistry in this work. This division was absolutely necessary if the book was to appear in a reasonable time; and moreover the nature and arrangement of a Dictionary enables various writers to co-operate in its production without material injury to the unity of the work.

We have been fortunate in securing the help of many contributors—English, American, and Foreign—whose work and position enable them to speak with authority on the subjects of which they treat.

We have had the advantage of the advice and assistance of Prof. G. Carey Foster, F.R.S., and Dr. W. J. Russell, F.R.S. To these gentlemen, and to all our contributors and abstractors, we return our sincere thanks.

Each editor contributes an introduction to his special part. It is hoped that the reader will not pass over these introductions, as they give the necessary explanations of the plan on which the book has been written. The table of abbreviations used is also important.

H. Forster Morley.
M. M. Pattison Muir.

March, 1888.

INTRODUCTION

TO THE PORTION OF THE BOOK DEALING WITH INORGANIC CHEMISTRY.

EACH element is described in its alphabetical position. The account of the element is ollowed by accounts of its binary compounds and those compounds which may be called ouble binary, in alphabetical order; *e.g. bromides, chlorides, chloriodides, sulphochlorides,* xc.; but *cyanides* are placed together in one article. There are also short articles on BROMIDES, CHLORIDES, OXIDES, &c.; and an article is devoted to each class of elements, *e.g.* ALKALI METALS, CARBON GROUP OF ELEMENTS, &c. Ammonium is treated as an element o far as the description of the AMMONIUM COMPOUNDS is concerned. Each group of salts, with he exception of those mentioned above, is described under one heading; *e.g.* all *carbonates* re described under the heading CARBONATES, all *nitrates* under the heading NITRATES, and o on. The salts of any specified metal are not as a rule enumerated in the article devoted to he metal; but in a section of this article is given a short account of the salts of the metal onsidered as a class. When some salts belonging to one class are marked off from the thers member of the class, a short article is devoted to a description of these salts as a whole, &c.; thus there is an article on ALUMS, and each alum is described in the article SULPHATES.

The nomenclature adopted is generally that used in the *Journal of the Chemical Society*, but it has not been thought expedient to attempt great strictness in this department. Structural formulæ are seldom used for inorganic compounds.

The term *molecular weight* is generally used only of those elements and compounds which have been gasified, and the specific gravities of which in the gaseous state have been determined.

The term *valency* is only applied to atoms, and is used to denote the maximum number of atoms of hydrogen, fluorine, chlorine, bromine, or iodine with which one atom of a specified element is known to combine to form a gaseous molecule.

The symbol Aq is employed to denote an indefinite quantity of water; when Aq is added to the symbol of an element or compound it means an aqueous solution of this body.

The following gentlemen have been so good as to prepare abstracts of the papers dealing with inorganic chemistry which have appeared in the various journals since the publication of the last supplement to the first edition of this Dictionary:—Messrs. Cosmo I. Burton, William Burton, G. J. Hill, H. A. Lawrance, Chas. Slater, and Alfred E. Tutton. I am much indebted to these gentlemen, and also to Miss Ida Freund, Lecturer in Chemistry at Newnham College, Cambridge, who prepared a translation of Prof. Ostwald's article on Affinity, and I beg to tender them my best thanks.

M. M. PATTISON MUIR.

INTRODUCTION

TO THE ARTICLES RELATING TO ORGANIC CHEMISTRY.

ORGANIC chemistry probably includes a greater number of observed phenomena than any other science; it is, clearly, not possible to arrange the description of these in such a way that any one, ignorant of the method of arrangement, could readily obtain the information he required. The reader is therefore requested to look through this introduction before referring to any of the organic articles.

The general idea is to devote a separate article to each compound and to arrange these articles in strictly alphabetical order; exceptions are made in the salts of acids and of bases, the ethers, chlorides, amides, anilides, and anhydrides of acids, the acetyl and benzoyl derivatives of compounds containing hydroxyl (OH), amidogen (NH_2), or imidogen (NH), the alkyl derivatives (ethers) of compounds containing hydroxyl, and the oxims and hydrazides of ketones and aldehydes; all these are described in the same article as the parent substance.

The headings of separate articles are in thick **BLACK CAPITALS**, the salts are in spaced type, the alkyl and alkoyl derivatives are in *spaced italics*; derivatives of derivatives are in spaced type. Subsidiary articles are in **black type**. In describing a compound the physical constants (e.g. melting-point, boiling-point, solubility, refractive index) are first given, then follow the modes of formation and preparation of the body, then such properties as cannot be expressed numerically, and finally a list of the chief reactions in which it plays a part. Inasmuch as organic substances are chiefly characterised by their melting or boiling points, it has been thought desirable to give these immediately after the name and formula of each compound, so that they may be most readily found. The melting-points are inclosed in square brackets, the boiling-points in round brackets. The modes by which salts, ethers, acid chlorides, and amides are formed from the parent acid are only given in particular cases or when the method used is not general; a similar remark applies to the acetyl- and benzoyl-derivatives of compounds containing hydroxyl or amidogen, and to the oxims and hydrazides of ketones and aldehydes. Information on the preparation and properties of such derivatives will be found in general articles.

Nomenclature.

Constitutional names are usually employed, except when the constitution of a body is doubtful; cross-references will be found under the trivial names. Many trivial names that have been almost universally adopted are nevertheless retained, e.g. aniline, aspartic acid, cinnamic acid, pyrocatechin, hydroquinone, resorcin.

The names of hydrocarbons usually end in *ene* or *ane*, of phenols in *ol*, of bases in *ine*, and of indifferent bodies in *in*.

In naming several *substituting alkyls*, that with less carbon comes first, and when there is an equal number of carbon atoms the unsaturated alkyl comes before the saturated: e.g. methyl-ethyl-succinic acid; phenyl-naphthyl-amine; allyl-propyl-malonic acid. Radicles containing a closed ring, however, precede fatty radicles, unless there is great danger of ambiguity; in the latter case cross-references will be given.

Ethers, acetyl and *benzoyl derivatives* of hydroxylic compounds are placed under the parent substance. Thus anisole and phenyl acetate are described under 'Phenol,' as its methyl ether and acetyl derivative respectively. So also methoxy-benzaldehyde is described under 'Oxy-benzoic aldehyde' as its methyl derivative.

Tetra-alkylated ammonium compounds are usually described under the tertiary amine from which they are derived. Thus phenyl-tri-methyl-ammonium iodide is described under 'di-methyl-aniline' as its methylo-iodide.

Acetyl and benzoyl derivatives of amines are described under the amines to which they belong; thus acetanilide is described under 'Aniline' as its acetyl derivative. Derivatives of aniline, methylamine, &c., containing other alkoyls are usually described as the anilide, methylamide, &c., of the acid from which they are derived; thus $C_6H_5.SO_2.NEtH$ is described as the ethylamide of 'Benzene sulphonic acid.'

Sulphonic and carboxylic acids (whenever they are so named) are represented as derivatives of the hydrocarbon, not of the radicle, thus $C_2H_2(CO_2H)_4$ is called ethane tetra-carboxylic acid, not acetylene tetra-carboxylic acid; and $C_2H_4(SO_3H)_2$ is called ethane di-sulphonic acid, not ethylene di-sulphonic acid.

When a compound contains several substituents they are named in the following order: *Chloro-*, *Bromo-*, *Iodo-*, *Cyano-*, *Nitro-*, *Oxy-*, *Amido-*, *Sulpho-*, *Carboxy-*. In choosing the naming group (i.e. the group that is not to be represented as a substituent, but in the termination of the name) the following is the order of preference: CO_2H, SO_3H, CHO, SH, OH and NH_2. Amidogen has precedence over hydroxyl in fatty compounds, but the reverse is the case with aromatic compounds; thus we say oxy-propyl-amine, but amido-phenol.

Examples: chloro-bromo-phenol, not bromo-chloro-phenol; chloro-nitro-oxy-benzoic acid, not nitro-chloro-oxy-benzoic acid, nor nitro-oxy-chloro-benzoic acid, nor oxy-chloro-nitro-benzoic acid, nor oxy-nitro-chloro-benzoic acid, nor chloro-oxy-nitro-benzoic acid; sulpho-benzoic acid, not carboxy-benzene sulphonic acid; amido-phenyl mercaptan, not sulphydro-phenyl-amine, nor sulphydro-aniline.

Prefixes indicating position.

The letters ω, α, β, γ, &c., are employed to denote the position of substituents in an open chain of carbon atoms. If the substituent is attached to the terminal carbon atom it is preceded by ω, while α, β, γ, indicate its attachment to the first, second, or third, atom of carbon reckoned along the chain from the terminal atom. There are at least two ends to an open chain; the end to be reckoned terminal is determined by the nature of the compound: in monobasic acids it is the carboxyl, in alcohols the group CH_2OH, and in general the group represented in the termination of the name. Thus $CH_2Cl.CHI.CHBr.CO_2H$ is called γ-chloro-α-bromo-β-iodo-butyric acid.

When α, β, γ, &c., are used in any other sense than that just explained, they are inclosed between brackets; e.g. (β)-naphthol.

Exo- indicates substitution in an open chain, *Eso-* denotes substitution in a ring; these prefixes are used when the exact position of the substituent is unknown. The prefixes *o-*, *m-*, *p-*, (*ortho*, *meta*, *para*) indicate isomerism of the di- derivatives of benzene (*v.* p. 454); *s-* and *u-* are employed as contractions for *symmetrical* and *unsymmetrical*. Thus *s*-di-phenyl-ethane is $C_6H_5.CH_2.CH_2.C_6H_5$ while *u*-di-phenyl-ethane is $(C_6H_5)_2CH.CH_3$.

In derivatives of quinoline (*B.*) signifies the benzene ring and (*Py.*) the pyridine ring. In anthracene, acridines, and azines (*B.*) signifies the benzene rings, (*A.*) denotes the central ring.

Alphabetical Order.

In determining the alphabetical order, the following prefixes are discarded: *mono-*, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, *hepta-*, *octo-*, &c., *per-*, *ortho-*, *meta-*, *para-*, *poly-*, *exo-*, *eso-*, *prim-*, *sec-*, *tert-*, *iso-*, *pseudo-*, *allo-*, *a-*, *β-*, *γ-*, *ω-*, *v-*, *n-*, *o-*, *m-*, *p-*, *ψ-*, *s-*, *c-*, *u-*, *i-*, (*B.*), (*Py.*), (*A.*), and all numbers. Of course when the entire name is numeral, *e.g.* hexadecane, hexane, &c., this rule does not hold. Thus di-bromo-benzene is in the same article as bromo-benzene; paraldehyde is associated with aldehyde, isobutyric acid with *n*-butyric acid, &c. The prefixes pyro- and proto- do not belong to this class.

The presence or absence of hyphens between parts of a name in no way affects its alphabetical position; thus 'Benzylidene' precedes 'Benzyl iodide.'

Formulæ.

Formulæ, to save space, are written as much as possible in one line. A portion of a formula inclosed in brackets is usually supposed to represent a group

of atoms more intimately connected with the groups represented by the preceding symbols, which are not in brackets, than with those following, e.g. $CH_2(CO_2H).CH_2.CO_2H$ is succinic acid. When numbers within square brackets follow a formula they refer to the substituents taken in the order in which they occur in the formula: thus $C_6H_3Br(NO_2)(CO_2H)[1:2:6]$ is used as an abbreviation for $C_6H_3Br(NO_2)(CO_2H)[Br:NO_2:CO_2H = 1:2:6]$. The system here adopted differs, therefore from that sometimes employed, according to which the above symbol would mean $C_6H_3Br(NO_2)(CO_2H)[CO_2H:Br:NO_2 = 1:2:6]$. Constitutional formulæ are looked upon by the majority of chemists as nothing more than a short way of indicating which atoms in a molecule are directly combined, and which are only indirectly combined with one another. The followers of Van 't Hoff and Wislicenus, however, suppose that constitutional formulæ can be constructed in the form of solid figures which give some notion of the actual relative positions of the atoms in a molecule. All agree that it is by the use of constitutional formulæ that the remarkable development of organic chemistry has been made, and that they cannot be abandoned until something better can be found to take their place.

It is not possible to find space for discussing the reasons which have led to the adoption of each constitutional formula; where these reasons are not given, a careful consideration of the methods of formation and the reactions of the compound will probably reveal them.

Special Articles.

In a few articles a number of compounds are grouped together, in violation of the foregoing rules. The longest of these are the articles on 'azo-' compounds. Other such articles are on the ammonia derivatives of 'Benzoic aldehyde,' on 'Benzil,' on the organic derivatives of 'Antimony,' 'Arsenic,' and 'Bismuth,' on 'Camphor' and on 'Cellulose.' The following general articles, amongst others, will also be found in this volume: 'Acids,' 'Alcohols,' 'Aldehydes,' 'Alkaloids,' action of 'Aluminium chloride,' 'Amides,' 'Amido-Acids,' 'Amines,' 'Analysis,' 'Anhydrides,' 'Aromatic Series' (see also 'Benzene'), 'Azo-colouring matters,' 'Diazo- compounds,' and 'Bromo- compounds.'

Contracted Expressions.

Since the date to which Watts had brought the record of chemical discovery, the number of organic compounds known has doubled, nevertheless the space allotted to them in the present dictionary is little more than a quarter of that devoted to organic chemistry in the original dictionary and its supplements. It is evident that there must be extreme compression, and this compels the free use of abbreviated expressions; it is hoped, however, that a reader who has once made himself acquainted with the nature of these abbreviations will find that they are very convenient. In the first place, the symbols of a few common reagents are used in the text with purely qualitative meaning, although when connected in an equation they are used in the ordinary sense. The great saving of space (about 200 pages) has compelled the use of this convention, which would be reprehensible under any other circumstances. The use of the contractions 'v. sl. sol.;' 'sl. sol.,' 'm. sol.,' 'v. sol.,' 'v. e. sol.,' and 'sol.,' for 'very slightly soluble in,' 'slightly soluble in,' 'moderately soluble in,' 'very soluble in,' 'very easily soluble in,' and 'soluble in,' enables solubilities to be given in the case of many hundred compounds where space would otherwise have compelled their omission. Of course these terms are vague; where numerical data have been determined, they are usually given in the dictionary, preceded by the letter S. Particular attention should be paid to the exact meaning of these numbers; they denote the number of grammes of a liquid or solid dissolved by a *hundred grammes* of the solvent, but the number of volumes of a gas dissolved by *one volume* of the solvent. Soluble, used as an adjective, the menstruum not being named, means soluble in water.

Constants.

Numerical constants are not given in the form $a + bt + ct^2$, &c., since such expressions not only take up a great deal of room, but are usually worthless, because slight errors of experiment produce an enormous effect upon the constants b, c, &c.; in such cases one or two actual observations, of a kind likely to be useful in identifying the substance, have usually been selected.

It is unfortunate that there is a want of uniformity among authors in the method of recording physical constants. *Specific gravities* are given by most authors without any mention of the temperature of the water that is taken as standard. Some take water at 0°, some at 4°, and others compare the substance with water at the same temperature as itself. Taking the specific gravity of water at 4° as unity, that at 21° will be ·998; that is to say, for a substance whose specific gravity is about 1 we may make an error of ·002 by assuming that the author used water at 4° as a standard, whereas he really used water at 21°. Under such circumstances it would be preposterous to give four places of decimals, and such indefinite specific gravities have been cut down to three decimal places, and even then the last figure is somewhat doubtful.

Heats of formation are usually calculated on the assumption that the heat of formation of 44 g. of carbonic acid is 96,960, and that of 18 grms. of water is 68,360; Stohmann, Rodatz, and Herzberg, however, use 94,000 and 69,000 respectively, hence their heats of formation are not directly comparable with those of other observers.

Molecular refraction is the value of the expression $M\left(\frac{\mu-1}{d}\right)$, where M is the molecular weight, μ the index of refraction, and d the specific gravity of the liquid at 20 compared with water at 4° (Landolt, *P.* 123, 595; Brühl, *A.* 200, 139). Other constants, such as $\left(\frac{\mu^2-1}{\mu^2+2}\right)\frac{M}{d}$, have also been used; these are of course not comparable with those first mentioned (*cf.* Brühl, *A.* 235, 1).

The specific rotation is given by most observers for a tube of liquid 100 mm. long, but many French chemists use a 200 mm. tube as a standard, and some even 50 mm. When the length of tube is stated it is easy to apply the correction, but when, as is often the case, an author does not give the length of tube, his numbers are indefinite.

The rotation measured for the neutral tint is of course not the same as that measured for the sodium line, yet authors occasionally fail to mention the kind of light employed. The angular rotation ought to be divided by the specific gravity of the liquid during the experiment, in order that the effect of equal weights of material may be compared; yet it is to be feared that many authors neglect to perform this division, and also to mention that they have not done it.

Authors frequently fail to state whether their *melting* and *boiling-points* have been corrected for the exposure of part of the stem of the thermometer. This may make a difference of 5°. The immersion of the whole of the mercury in the liquid or vapour is indicated by i.V.

References.

Where the same paper is referred to several times in the course of one article, the full reference is given once, and in other places there will be found the first letter or the first two letters of the author's name, inclosed within brackets; thus, if (Perkin, *C. J.* 45, 890) and (P.) are found in the same article, the (P.) is a contraction for (Perkin, *C. J.* 45, 890).

Short Article Expanded.

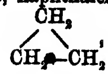
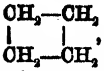
In order to make sure that the contractions employed are thoroughly understood, a short specimen article will be expanded by simply exchanging the contractions for their equivalents:—

Bromo-di-oxy-benzoic acid $C_6H_2Br(OH)_2CO_2H$ [x:2:6:1]. [184°, anhydrous]. From c-di-oxy-benzoic acid in ether and Br (Zehenter, *M.* 2, 480). Prisms (containing aq); v. sol. alcohol, v. sl. sol. water. Fe_2Cl_6 gives a violet colour to its aqueous solution.—AgA′aq.—BaA′$_2$7½aq.—KA′1½aq.

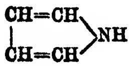
May be expanded thus:—

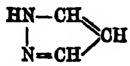
Bromo-di-oxy-benzoic acid $C_6H_2Br(OH)_2CO_2H$[Br:OH:OH:CO_2H = x:2:6:1] melts at 184° after it has been deprived of its water of crystallisation. It is formed, according to Zehenter (*Monatshefte*, vol. 2, p. 480), by adding bromine to an ethereal solution of *consecutive* di-oxy-benzoic acid. It crystallises in prisms, and the crystals contain one molecule of water of crystallisation to each molecule of the acid. These crystals are very soluble in alcohol, but very slightly soluble in water. Ferric chloride colours its aqueous solution violet. It forms the following salts $C_6H_2Br(OH)_2CO_2Ag,H_2O$; $\{C_6H_2Br(OH)_2CO_2\}_2Ba,7\frac{1}{2}H_2O$; and $C_6H_2Br(OH)_2CO_2K,1\frac{1}{2}H_2O$.

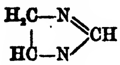
Nomenclature of Rings.

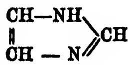
Besides the hydrocarbon rings, represented by benzene, naphthalene, phenanthrene, anthracene, indonaphthene $C_6H_4<{CH_2 \atop CH}>CH$, tri-methylene , tetra-methylene , penta-methylene $CH_2<{CH_2.CH_2 \atop CH_2.CH_2}>$, &c., there are a great many rings containing other elements. Some of these are collected here for convenience of reference. It will be noticed that glyoxaline and metapyrazole differ only in regard to the position of one atom of hydrogen. The exact structure of rings containing five or six atoms is not known; some alternative formulæ will be found on p. 446.

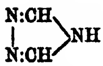
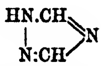
Nitrogen ring compounds.

 *Pyrrole* or *Pyrrol.*

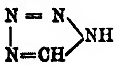
 *Pyrazole.*

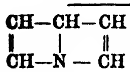
 *Metapyrazole.*

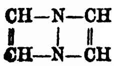
 *Glyoxaline.*

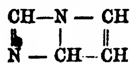
 or  *Triazole.*

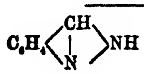
The di-oxy-derivative of the second form of triazol has been named 'Urazole' by Pinner.

 *Tetrazole.*

 *Pyridine.*

 *Pyrazine* (type of ketines).

 *Pyrimidine*

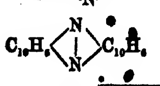


Indazine.

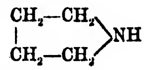
and $C_6H_4<{CH \atop NH}>N$ (pseudo)

$C_6H_4<{CH \atop NH}>CH$ *Indole.*

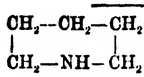
 *Phenazine.*

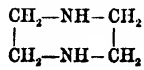
 *Naphthazine.*

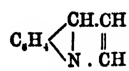
$C_6H_4<{NH \atop O}>C_6H_4$ *Phenazoxine*

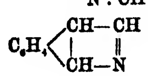
 *Pyrrolidine.*

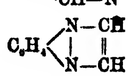
'Pyrroline' has been used by some authors for Pyrrole-dihydride. 'Pyrroline' in the abstracts in the *Journal of the Chemical Society* means Pyrrole.

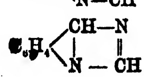
 *Piperidine.*

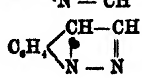
 *Piperazine.*

 *Quinoline.*

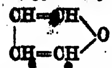
 *Isoquinoline.*

 *Quinoxaline.*

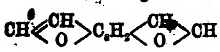
 *Quinazoline.*

 *Cinnoline.*

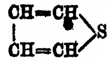
Oxygen ring compounds.

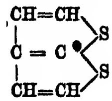
 *Furfurane.*

 *Coumarone.*

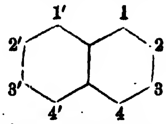
 *Benzodifurfurane.*

Sulphur ring compounds.

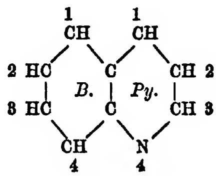
 *Thiophene.*

 *Thiophthene.*

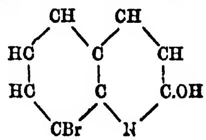
The numbers indicating position in compounds of naphthalene are as follows:—



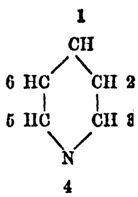
The positions 1, 4, 1′, 4′ are termed (α), while 2, 3, 2′, 3′ are called (β). Quinoline is numbered thus:—



Thus (*B.* 4)-bromo-(*Py-* 3)-oxy-quinoline would be



Pyridine is numbered thus:



One of the assumptions made by the recent doctrine of tautomerism is that a lactam CO.NH can readily change into a lactim C(OH):N, and that the group $CO.CH_2$ can change into C(OH):CH. It is obviously expedient to describe two compounds which are mutually interchangeable, if not identical, in the same article, hence rings containing CO.NH or $CO.CH_2$ are named as if they were hydroxylic compounds of the form C(OH):N and C(OH):CH.

Lactones and Anhydrides.

Lactones and anhydrides are usually described under the substance from which they may be derived by the abstraction of water; thus, butyro-lactone will be described under oxy-butyric acid.

Prefixes discarded.

The prefixes *homo-*, *hydro-*, and *mono-* are not used. The hydro- compounds of unsaturated bodies are, if saturated, named in the usual way; thus hydro-cinnamic acid is phenyl-propionic acid. The hydro- derivatives of ring compounds are described as hydrides of the simpler compounds from which they are derived: e.g. di-hydro phthalic acid as

phthalic acid dihydride. Compounds beginning with homo- must be re-named: thus homo-salicylic acid is oxy-toluic acid.

Hyphens.

Hyphens are placed between each significant part of a name; absence of the hyphen usually indicates close connection between two groups of atoms; e.g. phenylethylurea is $C_6H_5.C_2H_4.NH.CO.NH_2$ while phenyl-ethyl-urea is $C_6H_5NH.CO.NHC_2H_5$.

Ambiguous names.

A number of names have been used in several senses by different authors; it may therefore be well to mention the names chosen in some of these cases. The terms cyanide and isocyanide are altogether discarded, *carbamine* and *nitrile* being used instead. *Cyanate* is used for ordinary potassium cyanate and the ethers that may be derived therefrom; the corresponding sulphur compounds are described as *sulphocyanides* and *thio-carbimides* (mustard oils). *Cinnamyl* is $C_6H_5.CH:CH.CH_2$, the acid radicle $C_6H_5.CH:CH.CO$ being *cinnamoyl* and $C_6H_5.CH:CH$ is termed *styryl.*

Tolyl is used only for $CH_3.C_6H_4$. and not for benzyl $C_6H_5.CH_2$. nor for $CH_3.C_6H_4.CH_2$.

Cresyl is not used as a name. *Xylyl* is only used for $(CH_3)_2C_6H_3$., not for $CH_3.C_6H_4.CH_2$. nor for $(CH_3)_2C_6H_3.CH_2$. *Durene* is used as synonymous with tetra-methyl-benzene.

Discarded names.

As it commonly happens that several names have been given to the same compound, it may be well to give a list of the names that have been chosen in a few cases.

Carbamic ether	is used	instead of	*Urethane*
Urea	,,	,,	*Carbamide*
Thio-carbimide	,,	,,	*Mustard oil*
Tolylene	,,	,,	*Toluylene*
Methyl-pyridine	,,	,,	*Picoline*
Di-methyl-pyridine	,,	,,	*Lutidine*
Tri-methyl-pyridine	,,	,,	*Collidine*
Methyl-thiophene	,,	,,	*Thiotolene*
Di-methyl-thiophene	,,	,,	*Thioxene*
Oxy-pyridine	,,	,,	*Pyridone*
Methyl-quinoline	,,	,,	*Quinaldine*
Diquinoline	,,	,,	*Diquinolyl*
— hydrazide	,,	,,	*— izine*
(*B*. 1)-	,,	,,	*ana-*

Acknowledgments.

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H. Forster Morley.

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Articles by Mr. MUIR are initialed M. M. P. M

UNSIGNED ARTICLES are by Dr. MORLEY.

ABBREVIATIONS

I. Journals and Books.

When an author has been mentioned in an article, he is usually referred to thereafter in that article by his initial only.

A.	Liebig's Annalen der Chemie.
A. A.	Annales de la Sociedad Cientifica Argentina.
A. Ch.	Annales de Chimie et de Physique.
P. Am. A.	Proceedings of the American Academy of Arts and Sciences
Am.	American Chemical Journal.
Ann. M.	Annales des Mines.
Am. S.	American Journal of Science.
A. C. J.	Journal of the American Chemical Society.
Am. Ch.	American Chemist.
Am. J. Pharm.	American Journal of Pharmacy.
An.	The Analyst.
A. Ph. S.	Proceedings of the American Philosophical Society.
Ar. N.	Archives néerlandaises—The Hague.
Acad.	Mémoires de l'Académie des Sciences.
Ar. Ph.	Archiv der Pharmacie.
Ar. Sc.	Archives des Sciences phys. et nat.
B.	Berichte der deutschen chemischen Gesellschaft.
B. A.	Reports of the British Association.
Bl.	Bulletin de la Société chimique de Paris.
B. B.	Berliner Akademie-Berichte.
B. C.	Biedermann's Centralblatt für Agricultur-Chemie.
B. J.	Berzelius' Jahresberichte.
B. M.	Berliner Monatsberichte.
C. S. Mem.	Memoirs of the Chemical Society of London.
C. J.	Journal of the Chemical Society of London.
C. J. Proc.	Proceedings of the Chemical Society of London.
C. N.	Chemical News.
C. R.	Comptes-rendus hebdomadaires des Séances de l'Académie des Sciences Paris.
C. C.	Chemisches Central-Blatt.
D. P. J.	Dingler's polytechnisches Journal.
Fr.	Fresenius' Zeitschrift für analytische Chemie.
G.	Gazzetta chimica italiana.
G. A.	Gilbert's Annalen der Physik und Chemie.
H.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
I.	Proceedings of the Royal Irish Academy.
J.	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
J. C. T.	Jahresbericht für Chemische Technologie.
J. M.	Jahrbuch für Mineralogie.
J. de Ph.	Journal de Physique et des Sciences accessoires.
J. Ph.	Journal de Pharmacie et de Chimie.
J. pr.	Journal für praktische Chemie.
J. Th.	Jahresbericht über Thierchemie.
J. R.	Journal of the Russian Chemical Society.
J. Z.	Jenaische Zeitschrift für Medicin und Naturwissenschaft.
L. V.	Landwirthschaftliche Versuchs-Stationen.
M.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
M. S.	Le Moniteur Scientifique.
Mém. S. d'A.	Mémoires de la Société d'Arcueil.
Mém. B.	Mémoires couronnés par l'Académie de Bruxelles.

N.	Nature.
N. Ed. P. J.	New Edinburgh Philosophical Journal.
N. J. P.	Neuer Jahresbericht der Pharmacie.
N. R. P.	Neues Repertorium für die Pharmacie.
N. J. T.	Neues Journal von Trommsdorff.
N. Z. R.	Neue Zeitschrift für Rübenzuckerindustrie.
P. M.	Philosophical Magazine.
P.	Poggendorff's Annalen der Physik und Chemie.
P. B.	Beiblätter zu den Annalen der Physik und Chemie.
Pf.	Pflüger's Archiv für Physiologie.
Pr. E.	Proceedings of the Royal Society of Edinburgh.
Ph.	Pharmaceutical Journal and Transactions.
Ph. C.	Pharmaceutisches Central-Blatt.
Pr.	Proceedings of the Royal Society.
P. R. I.	Proceedings of the Royal Institution of Great Britain.
P. Z.	Pharmaceutische Zeitschrift für Russland.
R. T. C.	Recueil des travaux chimiques des Pays-Bas.
R. P.	Repertorium für die Pharmacie.
Q. J. S.	Quarterly Journal of Science.
S.	Schweigger's Journal der Physik.
Scher. J.	Scherer's Journal der Chemie.
S. C. I.	Journal of the Society of Chemical Industry.
Sitz. W.	Sitzungsberichte der K. Akademie zu Wien.
T. or *Tr.*	Transactions of the Royal Society.
T. E.	Transactions of the Royal Society of Edinburgh.
W.	Wiedemann's Annalen der Physik und Chemie.
W. J.	Wagner's Jahresbericht.
Z.	Zeitschrift für Chemie.
Zeit. ang. Ch.	Zeitschrift für angewandte Chemie.
Z. B.	Zeitschrift für Biologie.
Z. f. d. g. Naturwiss.	Zeitschrift für die gesammten Naturwissenschaften.
Z. K.	Zeitschrift für Krystallographie und Mineralogie.
Z. P. C.	Zeitschrift für physikalische Chemie.
Z. V.	Zeitschrift des Vereins für die Rübenzuckerindustrie des deutschen Reiches.
Bn.	Handbuch der organischen Chemie: von F. Beilstein, 2te Auflage.
E. P.	English Patent.
G. P.	German Patent.
Gm.	Gmelin's Handbook of Chemistry—English Edition.
Gm.-K.	Gmelin-Kraut: Handbuch der anorganischen Chemie.
Gerh.	Traité de Chimie organique: par Charles Gerhardt.
K.	Lehrbuch der organischen Chemie: von Aug. Kekulé.
G. O.	Graham-Otto: Lehrbuch der anorganischen Chemie [5th Ed.]
Stas, Rech.	Stas' Recherches, &c. } Aronstein's German translation is referred to as *Chem. Proport.*
Stas, Nouv. R.	Stas' Nouvelles Recherches, &c. }
Th.	Thomsen's Thermochemische Untersuchungen.

II. Terms and Quantities, &c., frequently used.

Aq	Water; *e.g.* NaOHAq means an aqueous solution of caustic soda.
aq	18 parts by weight of water.
A′, A″, A‴	Residues of mono-, di-, and tri-basic acids. Thus, in describing the salts of a monobasic acid NaA', CaA'_2, AlA'_3 may be written, HA' standing for the acid. For a dibasic acid we should write Na_2A'', CaA'', $Al_2A''_3$, &c.
B′ B″ &c.	Stand for bases of the ammonia type, in describing their salts. Thus the hydrochloride would be $B'HCl$ or $B''2HCl$, according as the base is monacid or diacid, &c.
conc.	Concentrated.
dil.	Dilute.
g.	gram.
mgm.	milligram.
mm.	millimetre.
mol.	molecule.

oil.	liquid, nearly, or quite, insoluble in water.
pp.	precipitate.
to ppt.	to precipitate.
ppg.	precipitating.
ppd.	precipitated.
sol.	soluble in.
insol.	insoluble in.
v. e. sol.	very easily soluble in.
v. sol.	very soluble in.
m. sol.	moderately soluble in.
sl. sol.	slightly soluble in.
v. sl. sol.	very slightly soluble in.
v.	see.
cf.	compare.
c.	about.
[°]	a melting-point.
(°)	a boiling-point.
H.	Hardness (of minerals).
At. w.	Atomic weight.
Mol. w. or M. w.	Molecular weight.
D.	Density.
cor.	corrected.
uncor.	uncorrected.
i.V.	in vapour.
V.D.	vapour-density, *i.e.* density of a gas compared with hydrogen or air.
S.G.	Specific gravity compared with water.
S.G. $\frac{10}{0}$	" " at 10° compared with water at 0°.
S.G. $\frac{15}{4}$	" " " 15° " " " " 4°.
S.G. ^{12}	" " " 12°; compared with water of which the temperature is not given.
S.H.	Specific heat.
S.H.v.	" " of a gas at constant volume.
S.H.p.	" " " " " pressure.
H.C.	Quantity of heat, in gram-units, produced during the complete combustion of the mass of a solid or liquid body represented by its formula, taken in grams.
H.C.v.	Heat of combustion in gram-units of a gram-molecule of an element or compound, when gaseous, under constant volume.
H.C.p.	The same, under constant pressure.
H.F.	Quantity of heat, in gram-units, produced during the formation of the mass of a solid or liquid body represented by its formula, taken in grams, from the masses of its constituent elements expressed by their formulæ, taken in grams.
H.F.v.	Heat of formation of a gram-molecule of a gaseous compound from the gram-molecules of its elements under constant volume.
H.F.p.	The same, under constant pressure.
H.V.	Heat of vaporisation of a liquid, *i.e.* gram-units of heat required to change a gram-molecule of the liquid compound at B.P. into gas at same temperature and pressure.
T.C.	Thermal conductivity (unit to be stated).
S.V.	Specific volume; or the molecular weight of a gaseous compound divided by the S.G. of the liquid compound at its boiling-point compared with water at 4°.
S.V.S.	Specific volume of a solid; or the mass of the solid expressed by its formula, taken in grams, divided by its S.G.
E.C.	Electrical conductivity (the unit is stated in each case).
C.E. (10° to 20°)	Coefficient of expansion (between 10° and 20°).
S.	Solubility in water: of a gas = volume dissolved by 1 volume of water; of a liquid or solid = number of grms. dissolved by 100 grms. of water. In both cases the temperature is stated.
S. (alcohol)	" " alcohol: of a gas = volume dissolved by 1 volume of water; of a liquid or solid = number of grms. dissolved by 100 grms. of water. In both cases the temperature is stated.
μ_β	Index of refraction for hydrogen line β.
μ_D, &c.	" " " sodium " D, &c.
$R_D \frac{15}{0}$	Molecular refraction for sodium light, *i.e.* index of refraction for line D minus one, multiplied by molecular weight, and divided by S.G. at 15° compared with water at 0°.
R_D	The same; S.G. being determined at 15°-20° and referred to water at 4°.
R_∞	The same for line of infinite wave-length, index being determined by Cauchy's formula (Brühl's R_A).

$[\alpha]_D$ . .	Specific rotation for sodium light.
$[\alpha]_j$ . .	„ „ „ neutral tint. $[\alpha] = \frac{100}{p} \times \frac{a}{d}$. a = observed rotation for 100 mm. of liquid. d = S.G. of liquid. p = no. of grammes of active substance in 100 grammes of liquid.
M. M	Molecular magnetic rotatory power $= \frac{m \times a}{d \times a' \times m'}$, where m = molecular weight of the body of S.G. $= d$, a = angle of rotation under magnetic influence, a' = angle of rotation of water under same influence, and m' = molecular weight of water (18).
Ac . .	Acetyl C_2H_3O.
Bz . .	Benzoyl C_7H_5O.
Cy . .	Cyanogen CN.
Et . .	Ethyl C_2H_5. (in formulæ)
Me . .	Methyl CH_3. (in formulæ)
Ph . .	Phenyl C_6H_5. (in formulæ)
Pr . .	Normal Propyl $CH_2.CH_2.CH_3$. (in formulæ)
Pr . .	Isopropyl $CH(CH_3)_2$. (in formulæ)
R, R' &c.	Alcohol radicles or alkyls.
prim . .	primary.
sec . .	secondary.
tert . .	tertiary.
n . . .	normal.
m, o, p .	meta—ortho—para.
c . . .	consecutive.
i . . .	irregular.
s . . .	symmetrical.
u . . .	unsymmetrical.
ψ . . .	pseudo.
ν . . .	attached to nitrogen.
α . . / β . . / γ . .	Employed to denote that the substituent is attached to a carbon atom which is next, next but one, or next but two, respectively, to the terminal carbon atom. The end to be reckoned from is determined by the nature of the compound. Thus $CH_3.CHBr.CO_2H$ is α-bromopropionic acid.
ω . . .	denotes that the element or radicle which follows it is attached to a terminal carbon atom.
α, β, γ, &c.	indicate position in an open chain, only.
1,2,3, &c.	indicate position in a ring only.
(α), (β), &c.	Used when α, β, &c. are employed in a sense different from the above, *e.g.* (α)-di-bromo-camphor.
	Baeyer's Nomenclature:
(*B.*) . .	benzene ring.
(*Py.*) . .	pyridine ring.
	Thus (*B.* 1:3) dichloroquinoline, means a meta-dichloroquinoline in which the chlorine atoms are both in the benzene ring. While (*Py.* 1:3) dichloroquinoline, means a similar body, only the chlorine atoms are in the pyridine ring. The numbers are counted from two carbon atoms which are in different rings, but both united to the same carbon atom.
(*A.*) . .	denotes the central ring in the molecule of anthracene, acridines, and azines.
eso- . .	means that the element or radicle it precedes is in a closed ring.
exo- . .	„ „ „ „ „ not in a benzene ring.
allo- . .	denotes isomerism that is not indicated by ordinary formulæ; thus maleic acid may be called *allo*-fumaric acid.
thio- . .	denotes displacement of oxygen by sulphur.
sulpho- .	„ the group SO_3H, except in the word sulphocyanide.
sulphydro-	„ the group SH.
—	Tribromonitrobenzene sulphonic acid [1:2:3:4:5] means that the three bromines occupy positions 1, 2, and 3; the nitro- group the position 4, and the sulpho- group the position 5.

* *Denotes that the formula to which it is affixed has not been determined by analysis. But it by no means follows that formulæ without this mark are those of analysed compounds.

All temperatures are given in degrees Centigrade unless when specially stated otherwise.

Wave-lengths are given in 10^{-7} mm.

Formulæ, when used instead of names of substances, have a qualitative meaning only.

Thomsen's notation is used in thermochemical data.

DICTIONARY OF CHEMISTRY

ABIES.—The needles of *A. pectinata* contain a sugar called *Abietite*, $C_6H_8O_3$, very much like mannite, but differing therefrom in composition and in solubility. The same plant contains a tannin identical with the soluble tannin of the horse-chestnut, $C_{18}H_{12}O_6$, and convertible by hydrochloric acid into an anhydride $C_{52}H_{46}O_{23}$, insoluble in cold water, but soluble in boiling potash-lye, slightly in water and alcohol (Rochleder, *J. pr.* 105, 63, 123).—The fruits of *Abies Reginæ Amaliæ*, indigenous in Arcadia, yield, by distillation with water, about 18 p.c. of a colourless volatile oil $C_{10}H_{16}$, smelling like lemons, S.G. ·868 (156–159°); slightly lævorotatory. Resinifies quickly in the air, exerting an ozonising influence stronger than that of turpentine-oil. Dissolves iodine, and absorbs hydrogen chloride, forming a liquid compound $C_{10}H_{16}.HCl$ (Buchner a. Thiel, *J. pr.* 92, 109). H. W.

ABIETENE C_7H_{16}.—The heptane of *Pinus sabiniana* (*v.* HEPTANES).

ABIETIC ACID $C_{44}H_{64}O_5$ [139°] or [165°].—Caillot, *J. Ph.* 16, 436; Maly, *A.* 129, 94; Emmerling, *B.* 12, 1441; Kelbe, *B.* 13, 888.—*Occurrence.* The clear liquid turpentine of various species of pine contains abietic anhydride $C_{44}H_{62}O_4$, which, on exposure to the air, absorbs moisture and is converted into abietic acid, the liquid then coagulating to an opaque granular pulp. The anhydride is the chief constituent of common resin or colophony.

Preparation.—1. Coarsely pounded colophony is digested for two days with weak spirit; the liquid is decanted from the white crystalline pulp, and squeezed in a press; the press-cake dissolved in hot strong alcohol, and the solution left to itself at ordinary temperatures; a white crystalline crust is thus obtained; the mother-liquor, when cooled by ice, usually solidifies to a loose mass of white laminæ, which constitutes the greater part of the product. The crystalline crust consists of sylvic acid $C_{20}H_{30}O_2$, the laminæ of abietic acid (M.).—2. Colophony is digested for two days with spirit of 70 p.c., and the undissolved portion, after washing with weak spirit, is dissolved in the smallest possible quantity of glacial acetic acid. From this solution the acid separates in crusts, and on adding a little water to its solution in hot alcohol and stirring, it is obtained in crystalline scales (E.).—3. Soda-lye which has been used for purifying crude resin-oil is mixed with common salt, and the soap which separates is dried at 70°–80°, and purified by exhaustion with ether. The residue dissolves in alcohol, and the solution, on evaporation, deposits needle-shaped crystals of sodium abietate, the aqueous solution of which yields, on addition of hydrochloric acid, a white pp. of abietic acid, which melts to a resinous mass if the mixture is boiled (K.).

Properties.—Separates from hot alcoholic solution in irregular transparent pointed triclinic crystals melting at 165° (M., K.); 139° (E.); 135° (Flückiger). Sol. alcohol, ether, benzene, glacial HOAc, $CHCl_3$ and CS_2.

Reactions.—1. Abietic acid distilled with *zinc chloride* yields a heavy oil (70°–250°) containing heptylene (E.).—2. Strong *hydrochloric* and *hydriodic acids* at 145° abstract the elements of water from it, leaving the anhydride (E.); but when treated in alcoholic solution with gaseous HCl, it yields sylvic and sylvinolic acids:

$$C_{44}H_{64}O_5 + H_2O = C_{20}H_{30}O_2 + C_{24}H_{36}O_4 \ (?)$$

Sylvic acid is also formed when a hot alcoholic solution of abietic acid is mixed with sulphuric acid (M.).—3. Triturated with PCl_5 it yields on distillation a volatile oil $C_{44}H_{60}$, called by Maly *abietone*, together with HCl and $POCl_3$.—4. By oxidation with $KMnO_4$, abietic acid yields carbonic, acetic and formic acids.—5. Boiled with *chromic mixture*, it yields large quantities of acetic and formic acids, and, after removal of these by distillation, ether extracts from the liquid a small quantity of trimellitic acid $C_6H_3(CO_2H)_3$ (E.).—6. The anhydride (colophony), oxidised with *nitric acid*, yields isophthalic acid, together with trimellitic acid (Schreder, *B.* 6, 413).—7. Abietic acid fused with *potash* yields propionic, but no protocatechuic, acid (M.).—8. *Sodium-amalgam* added to a warm alcoholic solution of abietic acid converts it into hydrabietic acid $C_{44}H_{68}O_5$, a dibasic acid, which forms white unctuous laminæ melting at 160° (M.).—9. Abietic acid with *acetic chloride* or *anhydride* at 160° yields an oily acetyl-compound (E.).—10. *Bromine* added to a solution of abietic acid in CS_2 forms a bromo-derivative, probably $C_{44}H_{62}Br_2O_5$, which separates from alcohol as a red powder melting at 134° (E.).—11. Distilled with *zinc dust* it yields toluene, *m*-ethyltoluene, naphthalene, methyl-naphthalene, and methyl-anthracene (Ciamician, *G.* 8, 305, *B.* 11, 269).

Salts.—Abietic acid is dibasic, mostly forming normal, rarely acid, salts. The alkaline salts are difficultly crystallisable. The normal abietates of the other metals $C_{44}H_{62}M''O_5$ are sparingly soluble in water, and are obtained by precipitation. Na_2A'', needles (from alcohol).—MgA'', flocculent, v. sol. alcohol.—MgH_2A_2''.—CaA''.—BaA''.—ZnA'', sl. sol. alcohol.—CuA'', v. sol. CS_2 or ether; pale green.

Ethyl Abietate Et_2A'', obtained by decomposing silver abietate with ethyl iodide diluted with ether, forms a yellowish mass, having an

etheric odour; insoluble in water, slightly soluble in alcohol, easily in ether and CS_2.

Abietin $C_{33}H_{74}O_8$ *i.e.* $C_{44}H_{81}(CHMe:CH)_2O_8$ is deposited from a mixture of glycerin and a concentrated alcoholic solution of abietic acid, after exposure to a low temperature for several days, in small white crystals melting at 125°, soluble in ether and alcohol (M.). H. W.

ABIETIC ANHYDRIDE $C_{44}H_{62}O_4$ is not formed by direct dehydration of the acid, but exists, as already observed, in the clear fresh turpentine of certain conifers, and forms the essential part of colophony. H. W.

ABIETIN. *V. supra.*

ABIETITE $C_4H_8O_3$.—*Abietol.* The sugar of *Abies pectinata.*

ABROTINE $C_{21}H_{22}N_2O$.—An alkaloid from *Artemisia abrotanum* (P. Giacosa, *J.* 1883, 1356). White crystalline powder or white needles. Sl. sol. hot water. Its solutions fluoresce blue. **Salts**: $B''H_2PtCl_6$.—$B_2''H_2SO_4$6aq. Needles.

ABSINTHIN or *Absynthiin* $C_{40}H_{56}O_9$ [120°-125°].—(Mein, *A.* 8, 61; Luck, *A.* 78, 87; Kromayer, *Ar. Ph.* [2] 108, 129).—The bitter principle of wormwood (*Artemisia absynthium*). Prepared by exhausting the dry herb with cold water; absorbing the bitter principle from the concentrated extract with boneblack; extracting with alcohol; purifying by treatment with basic lead acetate, precipitating the lead with H_2S, and evaporating the filtrate.

Properties.—Yellow powder, composed of minute crystals. V. sl. sol. cold water, sl. sol. hot water, v. sol. alcohol or ether. Very bitter. Neutral to litmus. Smells like wormwood.

Reactions.—1. Conc. H_2SO_4 forms a brown solution, turning greenish-blue. A little water turns the colour to a splendid blue, destroyed by more water.—2. Boiling dilute H_2SO_4 acquires a yellowish-green fluorescence, and deposits a brown resin.—3. Does not reduce Fehling's solution.—4. Gives a mirror with warm ammoniacal $AgNO_3$.—5. An alcoholic solution gives a sticky pp. with tannin.—6. Gives no pps. with metallic salts. H. W.

ABSINTHOL.—$C_{10}H_{16}O$ (195°) or (201°).—(Beilstein a. Kupffer, *B.* 6, 1183, *A.* 170, 290; Wright, *C. J.* 27, 1 and 319).—Isomeric with common camphor. Forms the essential principle of wormwood-oil, in which it is associated with a terpene (b.p. below 160°) and a deep-blue oil (270°-300°) identical with the blue chamomile oil examined by Kachler (*B.* 4, 36). Absinthol boils at 195° (B. and K.), at 200°-205° (W.), 217° (Gladstone). Differs essentially from camphor in chemical reactions, not being converted into camphoric acid by oxidation with nitric acid, nor into camphe-carboxylic acid, $C_{11}H_{16}O_3 = C_{10}H_{14}(OH).CO_2H$, by sodium and CO_2, and yielding with melting potash a large quantity of resin but no acid. Heated with P_2S_5 it yields cymene $C_{10}H_{14}$, and cymyl hydrosulphide $C_{10}H_{13}SH$, boiling at 230°-240° (W.). Cymene is also formed, though in smaller quantity, by treating absinthol with zinc chloride (W.). H. W.

ABSORPTION OF GASES BY LIQUIDS AND SOLIDS *v.* GASES.

ABSORPTION SPECTRA *v.* PHYSICAL METHODS: sect. OPTICAL.

ACACIN or *Acacia gum v.* ARABIN.

ACAJOU.—The pericarp of the nuts of the Acajou or Cashew-nut tree, *Anacardium occidentale*, growing in the West Indies and South America, contains a large quantity of a red-brown resinous vesicating substance, which may be extracted by ether, the solution when evaporated leaving a network of small crystals of anacardic acid soaked in an oily liquid called *cardol*, to which the resin owes its acrid properties (Städeler, *A.* 63, 137). A catechin $C_{42}H_{34}O_{16}$ [165°] may be got from acajou-wood (Gautier, *Bl.* 30, 568). H. W.

ACAROID RESIN.—Resin of *Xanthorrhea hastilis*, a liliaceous tree of Australia: also called resin of Botany Bay. Yellow, fragrant, soluble in alcohol, ether and caustic potash. The potash-solution treated with HCl deposits benzoic and cinnamic acids. Nitric acid readily oxidises it to picric acid. Yields on distillation phenol and small quantities of benzene and styrene (Stenhouse, *A.* 57, 84). By potash-fusion it gives *p*-oxy-benzoic acid, resorcin, and pyrocatechin (Hlasiwetz a. Barth, *A.* 139, 78). H. W.

ACECHLORIDE OF PLATINUM *v.* ACETONE.

ACECONITIC ACID $C_6H_6O_6$.—The ethyl ether is formed, together with the (probably isomeric) citracetic ether, by the action of sodium on ethyl bromo-acetate:

$$3EtC_2H_2BrO_2 + 3Na = Et_3C_6H_3O_6 + 3NaBr + H_3$$

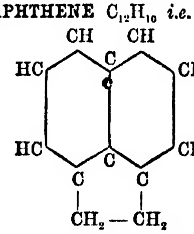
(Baeyer, *A.* 135, 306). The product is distilled *in vacuo*, and the ethers saponified by baryta. Baric acceconitate crystallises, leaving the gummy baric citracetate in solution.

Properties.—Nodular groups of needles. V. sol. ether. Gives no crystalline sublimate.

Salts.—Barium salt forms small, sparingly soluble crystals. A solution of the calcium salt becomes turbid when heated.—Ag_3A'''aq. *Ethyl ether.*—Et_3A'''. Lighter than water. H. W.

ACEDIAMINE $C_2H_6N_2$ *i.e.* $NH_2.CMe:NH$ *v.* ACET-AMIDINE.

ACENAPHTHENE $C_{12}H_{10}$ *i.e.* $C_{10}H_6:C_2H_4$,



M.w. 154. [95°] (Behr a. Dorp, *A*, 172, 265), [103°] (Schiff), (278° i. V.). V.D. 5·35 (for 5·33). S.V.S. 149·16 (Schiff, *A.* 223, 263).

Occurrence.—In coal-tar oil (Berthelot, *Bl.* [2] 8, 226).

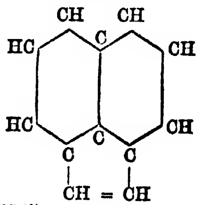
Formation.—1. By passing a mixture of ethylene and benzene or naphthalene through a red-hot tube (Berthelot).—2. By passing (α)-ethyl-naphthalene through a red-hot tube.—3. By treating (α)-ethyl-naphthalene with Br at 183° and decomposing the product, $C_{10}H_7.C_2H_4Br$, with alcoholic KOH at 100° (Berthelot a. Bardy, *C. R.* 74, 1463).

Preparation.—Heavy coal-tar oil (260°-290°) is carefully fractioned, and the fraction 260°-270° cooled strongly till it solidifies. Recrystallised from alcohol (Terrisse, *A.* 227, 184).

Properties.—Long needles (from alcohol). V. sol. hot alcohol, v. sl. sol. cold alcohol.

Reactions.—1. A mixture of alcoholic solutions of acenaphthene and *picric acid* deposits orange-yellow needles of the *picrate*, $C_{12}H_{10}.C_6H_2(NO_2)_3OH$ [162°].—2. Conc. H_2SO_4 forms a sulphonate whose salts are very soluble. A little HNO_3 turns the solution in H_2SO_4 green. 3. Cold HNO_3 forms *di-nitro-acenaphthene*. Yellow needles (from benzoline); insol. in alcohol.—4. CrO_3 and H_2SO_4 give naphthalic acid, $C_{10}H_6(CO_2H)_2$ (B. a. D.).—5. *Bromine* added to an ethereal solution forms *bromo-acenaphthene*, $C_{10}H_5BrC_2H_4$ [53°]; tables (from alcohol); oxidises to bromo-naphthalic acid (Blumenthal, *B.* 7, 1095).—6. A further quantity of *bromine* added to a solution in CS_2 forms $C_{12}H_8Br_6$; white needles (from alcohol).—7. *Iodine* at 100° polymerises it.—8. Conc. HI at 100° forms a hydrocarbon (? $C_{12}H_{12}$) (c. 270°).—9. Conc. HI (20 pts.) at 280° produces naphthalene di-hydride and ethane.—11. *Potassium* gives off hydrogen, forming $C_{12}H_9K$ (Berthelot).

ACENAPHTHYLENE $C_{12}H_8$ *i.e.* $C_{10}H_6:C_2H_2$; probably

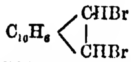


[93°] (265°–275°).

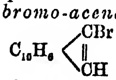
Preparation.—Acenaphthene (6g.) is put into a combustion tube, and the rest of the tube filled with litharge. The acenaphthene is heated strongly, and the vapours pass over the litharge, which must not be red hot (Blumenthal, *B.* 7, 1092; Behr a. Dorp, *B.* 6, 753).

Properties.—Large golden plates (from alcohol). Is partly decomposed by boiling. V. e. sol. alcohol, ether or benzene.

Reactions.—1. *Sodium amalgam* reduces it, in alcoholic solution, to acenaphthene.—2. *Chromic mixture* oxidises it to naphthalic acid.—3. Combines, in ethereal solution, with *bromine*, forming



[121°–123°]. This forms white needles (from benzene mixed with alcohol). Chromic mixture oxidises it to naphthalic acid. Alcoholic KOH converts it into *bromo-acenaphthylene*,



This is a liquid, but its picrate forms yellow needles. Bromo-acenaphthylene is converted by bromine into orange-red plates of di-bromo-acenaphthylene,

Picrate.—$C_{12}H_8C_6H_2(NO_2)_3OH$ [202°]. Yellow needles. V. sl. sol. cold alcohol.

ACETACETIC ACID *v.* ACETO-ACETIC ACID.

ACETAL $C_6H_{14}O_2$ *i.e.* $CH_3.CH(OEt)_2$.—*Di-ethyl-acetal, di-ethyl aldehydate* (*v.* ALDEHYDE). M.w. 118. (104°) (Stas); (103·2°) at 752 mm. (R. Schiff, *A.* 220, 104); (21°) at 22 mm., (50·5°) at 121 mm., (102·2°) at 760 mm. (Kahlbaum). S.G. $\frac{20}{4}$ ·8314 (Brühl); $\frac{15}{15}$ ·8319, $\frac{25}{25}$ ·8233 (Perkin); $\frac{103·2}{4}$ ·7364 (Sc.). V.D. 4·141. *Critical temperature* 254·4° (Pawlewski, *B.* 16, 2633). S. 4·6 at 25°. S.V. 159·88 (Sc.). μ_β 1·386. R_∞ 52·52 (B.). M.M. 6·968 at 16·1° (P.).

Occurrence.—In crude spirit, after filtering through charcoal (Geuther, *A.* 126, 63).

Formation.—1. By the imperfect oxidation of alcohol (Doebereiner; Liebig, *A.* 5, 25; 14, 156; Stas, *A. Ch.* [3] 19, 146; Wurtz, *A. Ch.* [3] 48, 370; *A.* 108, 84). Hence its occurrence in raw spirit and in old wines.—2. By action of chlorine on alcohol:

$$3C_2H_6O + Cl_2 = C_6H_{14}O_2 + 2HCl + H_2O.$$

3. One of the products of action of alcohol on ethyl di-bromo-acetate (Kessel, *B.* 11, 1917). 4. By passing non-inflammable PH_3 into a mixture of equal volumes of aldehyde and alcohol at −21° (R. Engel a. De Girard, *C. R.* 91, 692; *C. J.* 38, 458).

Preparation.—I. From Alcohol.—1. By imperfect oxidation under the influence of platinum-black. Fragments of pumice are moistened with nearly absolute alcohol in a wide-mouthed flask, the upper part of which is filled with shallow glass capsules containing platinum black, and the flask, covered with a glass plate is left in a room at 20° till nearly all the alcohol is converted into acetic acid. Alcohol of 60 p.c. is then poured in, and the flask, again covered with the glass plate, is exposed to the same temperature for a fortnight or three weeks, by which time the liquid above the pumice will have become viscid. This liquid is then poured off, more alcohol is added, and this course of proceeding is repeated till a few litres of very acid liquid have been obtained. This product is saturated with potassium carbonate, dried with calcium chloride, and about a fourth of it is distilled off; the distillate is treated with calcium chloride; the lower layer of liquid—consisting of aldehyde, ethyl acetate, and alcohol—is again mixed with calcium chloride, and distilled till the distillate no longer reduces silver nitrate; and the residue is treated with potash-lye, washed, dried with calcium chloride and rectified (Stas).—2. By distilling alcohol (2 pts.) with manganese dioxide (3 pts.), sulphuric acid (3 pts.), and water (2 pts.), and rectifying the product, which consists of acetal mixed with aldehyde, ethyl acetate, &c., as above.—3. By passing chlorine through alcohol of 80 p.c. cooled to between 10° and 15° till a portion becomes turbid on addition of water, indicating the formation of substitution-products. One fourth of the acid liquid is then distilled off; the distillate is neutralised with chalk; a fourth part again distilled off; and the distillate, consisting of alcohol, ethyl acetate, aldehyde, and acetal, is treated as above to separate the acetal (Stas). According to Lieben (*A. Ch.* [3] 52, 313), the chief products of the action of chlorine on 80 p.c. alcohol are mono- and di-chloracetal.

II. From Aldehyde.—1. By passing gaseous hydrogen chloride into a mixture of 1 vol. aldehyde and 2 vol. absolute alcohol, cooled by a freezing mixture, whereby the compound C_4H_9ClO is obtained, as an ethereal liquid floating on the

aqueous hydrochloric acid, and treating this compound with sodium ethylate:

$C_2H_4O + C_2H_6O + HCl = H_2O + C_4H_9ClO$;

and $C_4H_9ClO + C_2H_5ONa = NaCl + C_6H_{14}O_2$

(Wurtz a. Frapolli, *C. R.* 47, 418; *A.* 108, 223). 2. By treating aldehyde with PBr_3, whereby it is converted into ethylidene bromide, and acting on this compound with sodium ethylate:

$CHMeBr_2 + 2NaOEt = 2NaBr + CHMe(OEt)_2$

(W. a. P.).

Properties.—Colourless liquid, less mobile than ether, having a peculiar agreeable odour and refreshing taste, with an after-taste like that of hazel-nuts. Separated from aqueous solution by calcium chloride and other soluble salts. Miscible with ether or alcohol.

Reactions.—1. Not altered by mere exposure to *air*, but quickly oxidised in contact with *platinum-black* to aldehyde and acetic acid. Oxidised also by *nitric* and by *chromic acid.*—2. Not decomposed by caustic *alkalis* if air is excluded. 3. Forms substitution-products with *chlorine.* 4. Strong *sulphuric* and *hydrochloric acids* dissolve and decompose it, the mixture turning black.—5. *Dilute acids*, even in the cold, split up acetal into alcohol and aldehyde.—6. A solution of acetal does not give the iodoform reaction, unless it be first acidified (Grodzki, *B.* 16, 512). 7. PCl_5 forms $CH_3.CHCl.OEt$, EtCl and $POCl_3$ (Buchanan, *A.* 218, 38).—8. Heated with glacial HOAc it forms acetic ether, thus:

$CH_3.CH(OEt)_2 + 2AcOH =$
$CH_3CHO + H_2O + 2AcOEt.$

9. Does not reduce $AgNO_3Aq$.—10. *Chromic mixture* forms acetic acid.—11. Heated with MeOH it is almost completely converted into EtOH and $CH_3CH(OMe)_2$.—12. Heated with PrOH it is mostly unchanged, but some $CH_3.CH(OEt)(OPr)$ and some $CH_3CH(OPr)_2$ are formed.—13. Heated with *iso-amyl alcohol* it behaves as in 12.

References.—Homologues of acetal are described under the aldehydes, to which they correspond. Bromo- and chloro-acetals are described under bromo- and chloro-acetic aldehyde. For oxy-acetal *v.* glycollic aldehyde.

ACETALDEHYDE *v.* ALDEHYDE.

ACETAMIDE C_2H_5NO *i.e.* NH_2Ac or $CH_3.CONH_2$.—Amide of acetic acid. M.w. 59. [83°] (Hofmann, *B.* 14, 2729) (222° cor.). S.G. $\frac{4}{4}$ 1·159 (Schröder, *B.* 12, 562). R_∞ 24·35 in a 34-p.c. aqueous solution (Kanonnikoff, *J. pr.* [2] 31, 347). Discovered by Dumas, Malaguti, and Leblanc in 1847 (*C. R.* 25, 657).

Formation.—1. By heating ethyl acetate with strong aqueous ammonia at 120°

$AcOEt + NH_3 = AcNH_2 + HOEt.$

2. By action of ammonia on acetic anhydride:

$Ac_2O + 2NH_3 = NH_2Ac + AcONH_4.$

3. By distillation of ammonic acetate:

$AcONH_4 = AcNH_2 + H_2O$ (Kundig, *A.* 105, 277).

4. When dry NaOAc (580 g.) is distilled with NH_4Cl (225 g.) very little acetamide (70 g.) is got: the distillate is chiefly NH_3 and acid ammonic acetate, which boils at 145°.

Preparation.—1. Acetic ether and aqueous ammonia are left in a closed vessel until the ether has disappeared. The product is distilled.—2. Glacial acetic acid (1 kilo.) is saturated with dry NH_3 and the product distilled in a current of dry NH_3. Above 190° acetamide (460 g.) comes over; the first distillate (below 190°) is treated in the same way: it gives more acetamide (170 g.). A third repetition of this operation gives more acetamide (110 g.). Total yield: 740 g. (Keller, *J. pr.* [2] 31, 364).—3. Ammonic chloride and sodic acetate are heated in an enamelled iron digester for six hours at 230°. The product is distilled (Hofmann, *B.* 15, 981).—4. A mixture of ammonic acetate (20 g.) and acetic anhydride (26 g.) yields on distillation 96 p.c. (12 g.) of acetamide (Schulze, *J. pr.* [2] 27, 512).—5. Ammonic sulphocyanide (1 mol.) is boiled for four days with glacial acetic acid ($2\frac{1}{2}$ mols.):

$NH_4CNS + 2AcOH = 2AcNH_2 + COS + H_2O$ (S.).

Purification.—Acetamide can be freed from ammonic acetate by drying over lime (Menschutkin, *J. R.* 17, 259).

Properties.—White hexagonal scales, smelling like excrement of mice. Deliquescent. V. e. sol. water. Conducts electricity and is easily electrolysed.

Reactions.—1. Resolved by distillation with P_2O_5 into water and acetonitrile, C_2H_3N.—2. With P_2S_5 it also yields acetonitrile, giving off H_2S, and leaving a blackish tumefied residue.—3. Heated in dry HCl-gas it yields: *a.* A liquid distillate consisting of acetic acid with a small quantity of acetyl chloride; *b.* A crystalline distillate of $(C_2H_5NO)_2HCl$, and a compound of acetamide and diacetamide $C_2H_5NO.C_4H_7NO_2$, the latter of which may be dissolved out by ether; *c.* A non-volatile residue of acetamidine hydrochloride mixed with sal-ammoniac:

$2C_2H_5NO + HCl = C_2H_6N_2.HCl + C_2H_4O_2.$

(Strecker, *A.* 103, 328).—4. Acetamide heated in sealed tubes with saturated *hydriodic acid* yields ammonia, acetic acid, and ethane:

$2C_2H_5NO + 3H_2 = C_2H_4O_2 + 2NH_3 + C_2H_6$

(Berthelot, *Bl.* [2] 9, 183).—5. With CS_2 at about 210° it gives off H_2S, COS, CO, and probably ethane, leaving ammonium sulphocyanide mixed with undecomposed acetamide:

$2C_2H_5NO + CS_2 = NH_4.SCN + COS + CO + C_2H_6$

(Ladenburg, *Z.* [2] 4, 651). *V.* ALDEHYDES.—6. Nascent hydrogen (copper-zinc couple or sodium-amalgam) forms some alcohol and aldehyde (Essner, *Bl.* [2] 42, 98).—7. Heated with NaOEt at 180° it forms ethylamine (Seifert, *B.* 18, 1357).—8. With *ethyl orthoformate* at 180° acetamide yields ethyl alcohol and diacetyl-formamidine:

$2NH_2Ac + CH(OEt)_3 = 3EtOH + N_2(CH)Ac_2H.$

Another reaction, however, takes place at the same time, producing alcohol, ethyl acetate, and formamidine:

$2NH_2Ac + CH(OEt)_3 =$
$EtOH + 2EtOAc + N_2(CH)H_3$

(Wichelhaus, *B.* 3, 2).—9. Acetamide heated in sealed tubes with *benzaldehyde* is converted into benzylidene-diacetamide:

$2NH_2Ac + PhCOH = H_2O + PhCH(NHAc)_2.$

With *aldehyde* in like manner, it yields $MeCH(NHAc)_2$ in large prisms [169°], partly decomposed by distillation, and giving off aldehyde when treated with acids (Tawildarow, *B.* 5, 477). With *anisaldehyde* the compound $C_{12}H_{16}N_2O_3$ is formed in nodular groups of needles [180°], soluble in water, insoluble in alcohol and ether, decomposed by HCl, not altered by boiling with potash (Schuster, *Z.* [2] 6, 681). With *salicylic aldehyde* a yellow neutral body is formed (Cred-

ner, *ib.* 80). With *chloral* acetamide unites directly, forming the crystalline compound $C_2H_5NO.C_2HCl_3O$. (*v.* CHLORAL).—10. Heated with mesityl oxide it forms a basic substance, $C_8H_{13}NO$, '*oxy-hydro-collidine*.' A yellowish liquid (175°-180°) (Canzoneri a. Spica, *G.* 14, 349).

Combinations. — Acetamide unites directly with the stronger acids. The *hydrochloride* $(NH_2Ac)_2HCl$ is formed by passing gaseous HCl into its solution in ether-alcohol. Long needles (from alcohol); insol. in ether.—NH_2AcHCl (Pinner a. Klein, *B.* 10, 1896).—The *nitrate*, NH_2AcHNO_3 [98°], separates from a solution of acetamide in strong HNO_3. It is very acid, and is deliquescent. Sl. sol. ether. Gives off CO_2, N_2O and HNO_3 when heated.

Salts.—AcNHAg. Scales.—$(AcNH)_2Hg$. Six-sided prisms [195°]. Both formed by dissolving the oxides in acetamide.—$(AcNH)_2Zn$. From $ZnEt_2$ and acetamide. Amorphous. (Frankland.)

Chloro-acetamides.—The amides of the chloro-acetic acids are described under those acids. *Aceto-chloro-amide* NAcClH [110°] is formed by passing chlorine into fused acetamide, or by pouring aqueous HCl upon aceto-bromo-amide:

$$2NAcBrH + HCl = NAcClH + NAcH_2 + Br_2$$

(Hofmann, *B.* 15, 410). Sol. ether. Split up by HCl into chlorine and acetamide.

Bromo-acetamides *v.* BROMO-ACETIC ACIDS.

Aceto-bromo-amide

NHBrAc [108°]. NHBrAc aq. [70°-80°]. Formed by adding aqueous KOH to a solution of Br (1 mol.) in acetamide (1 mol.). Striated rectangular plates (from ether).

Reactions.—1. Boiled with *water* it forms acetamide, Br, HBrO, methyl-acetyl-urea, and methylamine.—2. Heated with Ag_2CO_3 it forms methyl cyanate:

$$2CH_3CO.NHBr + Ag_2CO_3 =$$
$$2CH_3NCO + 2AgBr + CO_2 + H_2O.$$

3. Boiled with KOHAq it forms HBr, CO_2, and methylamine, the methyl cyanate formed according to the last reaction being decomposed in the usual way.—4. Acetamide and NaOHAq form methyl-acetyl-urea.—5. *Ammonia* reacts violently, thus:

$$3NAcHBr + 5NH_3 = 3NAcH_2 + 3NH_4Br + N_2.$$

6. *Aniline* forms acetanilide and tri-bromo-aniline.—7. *Phenol* gives tri-bromo-phenol and acetamide (Hofmann, *B.* 15, 407).

Salts.—NAcBrNa. Hair-like needles, ppd. by conc. NaOH. $NAcBrNaBr_2aq$. Made by adding conc. NaOH to a mixture of acetamide (1 mol.) and bromine (1 mol.). Rectangular plates. Decomposed by water into NaBr and aceto-di-bromo-amide.

Aceto-di-bromo-amide $NAcBr_2$ [100°]. Made by adding aqueous KOH to a dilute solution of bromine (1 mol.) and bromo-acetamide (1 mol.) (Hofmann, *B.* 15, 413). Golden needles or plates; sol. warm water, alcohol, or ether. Boiled with water, it gives HBrO, NAcBrH, and $NAcH_2$. Potash decomposes it into nitrogen, acetic acid and potassic hypobromite. H. W.

Bromo-chloro-acetamide *v.* CHLORO-BROMO-ACETIC ACID.

Iodo-acetamide *v.* IODO-ACETIC ACID.

Di-acetamide NAc_2H. M.w. 180 [82°] (210°-215°).

Preparation.—1. The ethereal solution of the crystalline compound of acetamide and di-acetamide got by heating acetamide in a current of HCl (*v. Reaction* 3), deposits, when gaseous HCl is passed through it, spicular crystals of acetamide hydrochloride, and the filtrate yields, by evaporation over H_2SO_4, crystals of diacetamide.—2. By heating acetonitrile with glacial HOAc, or acetamide with Ac_2O at 250° (Gautier, *Z.* 1869, 127).—3. By boiling methyl-acetyl-urea with Ac_2O (Hofmann, *B.* 14, 2731).

Properties. — Long needles (from ether). Neutral. V. e. sol. water, v. sol. alcohol or ether. Does not combine with acids, so that HCl gives no pp. in an ethereal solution.

Reactions.—1. By boiling with *acids* or by heating with $ZnCl_2$ it is resolved into acetic acid and acetonitril.—2. Fuming HNO_3 reacts, giving off N_2O. H. W.

Tri-acetamide NAc_3 [79°].—Formed in small quantity when a mixture of acetic anhydride and acetonitrile is heated to 200°, and may be dissolved out by ether after the excess of Ac_2O has been distilled off. White flexible needles [78°-79°]. Neutral. Gently warmed with silver oxide it yields silver acetate; so likewise do acetamide and diacetamide (Wichelhaus, *B.* 3, 847). H. W.

Tri-acet-di-amide $N_2Ac_3H_3$ [212°-217°]. — This is the compound of acetamide and di-acetamide mentioned under acetamide (*Reaction* 3) and di-acetamide (*Preparation* 1).

Di-azo-acetamide *v.* AZO COMPOUNDS.

Ethyl-acetamide *v.* ETHYL-AMINE.

Methyl-acetamide *v.* METHYL-AMINE.

Phenyl-acetamide *v.* ANILINE.

ACET-.—If compounds whose names begin with *acet* or *aceto* are not here described, remove this prefix and look for the remaining word, changing the termination *ide*, if present, into *ine*.

ACETAMIDINE $C_2H_6N_2$ *i.e.* $CH_3.C(NH).NH_2$ *Acediamine, Ethenyl-amidine, Acet-imid-amide* (Strecker, *A.* 103, 328; Hofmann, *B.* 17, 1924).—The hydrochloride of this base is left as a residue when acetamide is distilled in a current of HCl (*v.* ACETAMIDE, *Reaction* 3). The mass is extracted with alcohol, which leaves NH_4Cl behind.

Properties.—When liberated from solutions of its salts, it splits up into ammonia and ammonic acetate.

Salts. – B'HCl: prisms (from alcohol), [165°]. —$(B'HCl)_2PtCl_4$: yellowish-red prisms. —$B'_2H_2SO_4$: pearly laminæ.

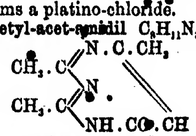
Reactions.—1. The hydrochloride boiled with Ac_2O and NaOAc for $1\frac{1}{2}$ hours forms anhydro-di-acetyl-acet-amidine and anhydro-di-acetyl-acet-amidil (Pinner, *B.* 17, 173).—2. *V.* ACETO-ACETIC ETHER, *Reaction* 25.

Anhydro-di-acetyl-acetamidine $C_6H_8N_2O$ [253°].—Prepared as just stated, the product being treated with aqueous NaOH and the pp. boiled with water, which dissolves the 'amidil,' but not the amidine.

Silky needles (from alcohol). Insol. water, sl. sol. cold alcohol, v. sol. hot alcohol, v. e. sol. dilute acids. Forms a platino-chloride.

Anhydro-di-acetyl-acet-amidil $C_6H_{11}N_3O2aq.$

Possibly



[185°]. Obtained as above. Nodules of small

prisms. Loses 2aq over H_2SO_4. Sl. sol. cold water, v. sol. hot water, v. e. sol. alcohol and in dilute acids. Forms a platinum salt.

ACETAMIDOXIM *v.* ETHENYL-AMIDOXIM.

ACETANILIDE *v.* ANILINE *Acetyl derivative.*

ACETIC ACID $C_2H_4O_2$ *i.e.* $CH_3.CO.OH$ or AcOH.—*Methane carboxylic acid, Pyroligneous acid.*—M.w. 60 [16·5°] (Zander), [17·5°] (Sonstadt, *C. N.* 37, 199). (118·29°) (Z.), (117·5°) (Schiff.). *Critical temperature* 321·5° (Pawlewsky, *B.* 16, 2684). S.G. *Solid.* $\frac{0}{0}$ 1·0701 (Z.); $\frac{15}{4}$ 1·0607 (Mendeléeff, *J.* 1860, 7). S.G. *Liquid.* $\frac{12.5}{4}$ 1·0576, $\frac{16}{4}$ 1·0543, $\frac{19}{4}$ 1·0503 (Pettersson, *J. pr.* [2] 24, 301); $\frac{20}{4}$ 1·0495 (Brühl); *at boiling-point* ·9325 (Ramsay, *C. J.* 35, 463). V.D. 29·7 at 250° and upwards. C.E. (0°–10°) ·00106 (Z.). H.F.p. 105,290. H.F.v. 104,130. S.H. (between 0° and 100°) ·497. Latent heat of fusion for 1 mol. (at 1·5° to 4·2°) 2619. μ_β 1·3765. R_∞ 20·69 (B.). M.M. 2·525 (Perkin). S.V. 64·3 (R.).

Occurrence.—In the juices of plants, especially of trees, and in certain animal secretions.

Synthesis.—1. From acetylene (*i.e.* from C and H) by converting that hydrocarbon into ethylene by direct addition of hydrogen, then the ethylene into alcohol, and oxidising the alcohol; or more simply by heating acetylene dichloride with aqueous potash at 230° or with alcoholic potash at 100° for ten hours:

$$C_2H_2Cl_2 + 3KHO = C_2H_3O_2K + 2KCl + H_2O$$

(Berthelot, *Z.* [2] 5, 683).—2. When a mixture, 1 vol. acetylene and 2 vols. air, is exposed to daylight over dilute potash-lye, the acetylene is slowly oxidised to acetic acid, which is absorbed by the alkali: $C_2H_2 + O + KOH = C_2H_3O_2K$ (Berthelot, *A. Ch.* [4] 23, 212).—3. From sodium-methyl and carbonic acid:

$$CH_3Na + CO_2 = CH_3.CO_2Na$$

(Wanklyn, *A.* 111, 234).—4. By boiling acetonitrile (methyl cyanide) with potash:

$$CH_3CN + KOH + H_2O = CH_3CO_2K + NH_3$$

(Frankland a. Kolbe, *A.* 65, 298).—5. By passing CO over sodium methylate at 160°:

$$CH_3ONa + CO = CH_3CO_2Na$$

(Fröhlich, *A.* 202, 294).

Formation.—1. By dry distillation of organic bodies, especially wood.—2. By the action of atmospheric oxygen, chromic acid, nitric acid, hypochlorous acid, and other oxidisers, on alcohols and other organic bodies, especially under the influence of ferments which act as carriers of oxygen.—3. By the action of KOH or NaOH at a high temperature on various organic bodies, *e.g.* tartaric, citric, and malic acids, sugar, alcohol, &c.—4. In various processes of fermentation and putrefaction (*J.* 1878, 1017, 1019, 1023).

Preparation.—1. By oxidation of ethyl alcohol, the alcohol being first converted into aldehyde: $C_2H_6O + O = H_2O + C_2H_4O$, and the aldehyde then oxidised to acetic acid. The oxidation may be effected:

a. By the influence of *spongy platinum.* If a tray containing this substance be placed over a dish containing a little alcohol, the whole being covered with a bell-glass open below, as well as at the top, on gently warming the dish the alcohol will be rapidly oxidised, acetic acid condensing in abundance on the inside of the jar. Much of the alcohol is, however, converted into aldehyde and lost by volatilisation.

b. Under the influence of *ferments.* This is the ordinary process of making vinegar from alcoholic liquids, wine being generally used for the purpose in France and Germany, and malt in England. The most favourable temperature is 25°–30°. The experiments of Pasteur have shown that the oxidation of alcohol in the ordinary process of vinegar-making depends essentially on the presence of a fungoid plant called *Mycoderma vini, Mycoderma aceti*, or 'mother-of-vinegar,' and is invariably preceded by its development on the surface of the liquid. It appears to act like platinum-black, as a carrier of oxygen. The plant may be sown on the surface of the liquid by introducing a small portion of it from another vinous liquid already in the fermenting state, or by simply exposing the liquid to the air in which the germs of this fungus, as of many others, are always floating. Like all other plants, it requires food for its development, and this it finds in the albuminous matter and mineral salts contained in ordinary vinous liquors. If these are absent the plant cannot grow, and acetification cannot take place. Thus, pure aqueous alcohol may be exposed to the air for any length of time without turning acid, because the germs of the mycoderma which fall into it from the air remain barren for want of nutriment. Moreover, pure aqueous alcohol may be acetified without the aid of any albuminous matter, provided the mycoderma have access to it, and be supplied with the nitrogen and saline matters necessary for its growth. Pasteur has in fact shown that this nutriment may be supplied in the form of alkaline and earthy phosphates and ammonium phosphate, the latter furnishing the nitrogen. Under these circumstances the mycoderm grows, though less quickly than in ordinary vinous liquids, and the alcohol is slowly converted into acetic acid. If the mycoderma be allowed to remain in the liquid after the acetification is complete, the whole of the acetic acid may be destroyed and the liquid rendered perfectly neutral. (Pasteur, *Études sur le Vinaigre*, Paris, 1868; also *Annales Scientifiques de l'École normale supérieure*, tome i. 1864; *Bl.* 1861, p. 94; *J.* 1861, 726.)

Malt Vinegar is prepared from a fermented wort obtained by mashing malt, or a mixture of malt and raw barley, with water, as in brewing.

Quick Vinegar Process.—The oxidation of the alcoholic liquor may be greatly accelerated by allowing it to trickle down in a fine shower over chips of wood covered by the mycoderma, and exposed to an upward current of air.

Wood Vinegar—Pyroligneous Acid.—The greater part of the acetic acid now used in arts and manufactures is obtained by the destructive distillation of wood. The wood is heated in large iron cylinders connected with a series of condensers. The watery liquid which condenses in the receivers, consisting of water, tar, methyl alcohol or wood-spirit, methyl acetate and acetic acid, is redistilled after separation of the tar, the wood-spirit passing over among the first portions of the distillate and the acetic or pyroligneous acid afterwards. The acid thus obtained is coloured and has a strong tarry flavour,

not removable by distillation. To purify it, the crude liquor is saturated with lime, which removes part of the tarry matter, the rest remaining in solution with the calcium acetate. The liquid, clarified by repose or by filtration, is evaporated in an iron pot to half its bulk, and mixed with enough hydrochloric acid to give a slight acid reaction, whereupon the greater part of the tarry matter separates, and may be skimmed off the surface. The hydrochloric acid also decomposes certain compounds of lime with creosote and other volatile substances, which may then be expelled by heat. The calcium acetate thus purified is completely dried and distilled with hydrochloric acid. The density of the acetic acid thus obtained is about 1·06. If it contains hydrochloric acid it may be purified by redistillation with addition of a small quantity of sodium carbonate, or, better, 2 or 3-p.c. potassium dichromate, this latter at the same time destroying certain organic impurities which give the acid a peculiar odour (Völckel, *A.* 82, 49). Crude wood vinegar contains small quantities of propionic, *n*-butyric, *n*-valeric, and two crotonic acids (Grodzki a. Krämer, *B.* 11, 1356).

Crystallisable or *Glacial Acetic Acid* —the pure acid, $C_2H_4O_2$, so-called because it crystallises at ordinary temperatures—is obtained: 1. From the ordinary aqueous acid by fractional distillation, repeated till the residue solidifies on cooling. 2. By distilling certain dry metallic acetates with strong sulphuric acid or with hydrogen potassium sulphate,

$$2C_2H_3KO_2 + H_2SO_4 = K_2SO_4 + 2C_2H_4O_2;$$
$$\text{and } C_2H_3KO_2 + HKSO_4 = K_2SO_4 + C_2H_4O_2.$$

3. Together with acetone and other products, by dry distillation of cupric acetate (*Spiritus Æruginis* or *Sp. Veneris*).

Physical Properties.—The solid acid forms prismatic or tabular crystals. The liquid acid is transparent, colourless, and mobile. Vapour-density at 250° and upwards is 2·08 (air = 1) or 29·7 (H = 1), which is nearly half the molecular weight of the acid, showing that at these high temperatures the vapour exhibits the normal condensation. But at temperatures nearer to the boiling-point the density of the vapour is much greater, showing a condensation to $\frac{2}{3}$ vol. or even less (Cahours, *C. R.* 19, 771; 20, 51). The pressure of the vapour of solid acetic acid is 1·3 mm. at −5·7°, 2·0 mm. at 0°, and 9·5 mm. at 16·4°; the vapour-pressure of liquid acetic acid being 3·2 mm. at 0°, 6·3 mm. at 10°, 11·8 mm. at 20°, 19·9 mm. at 30° (Ramsay a. Young, *C. J.* 47, 45).

Glacial acetic acid has a pungent sour taste and odour and blisters the skin. It does not redden litmus paper *per se*, but reddens it strongly when mixed with water. It does not attack $CaCO_3$ until water is added. It is hygroscopic.

Aqueous Acid.—Acetic acid mixes with water in all proportions. The density of the aqueous acid does not vary in proportion to the amount of real acid present; and consequently the strength of any sample cannot be inferred from its density, but must be determined by titration with standard alkali. The following table has been constructed in this manner by Oudemans (*Fr.* 5, 452) for the temperatures 0°, 15°, and 40°.

Density of Aqueous Acetic Acid (Oudemans).

$C_2H_4O_2$ p. c.	Density at 0°	Density at 15°	Density at 40°
0	0·9999	0·9992	0·9924
1	1·0016	1·0007	0·9936
2	1·0033	1·0022	0·9948
3	1·0051	1·0037	0·9960
4	1·0069	1·0052	0·9972
5	1·0088	1·0067	0·9984
6	1.0106	1·0083	0·9996
7	1·0124	1·0098	1·0008
8	1·0142	1·0113	1·0020
9	1·0159	1·0127	1·0032
10	1·0176	1·0142	1·0044
11	1·0194	1·0157	1·0056
12	1·0211	1·0171	1·0067
13	1·0228	1·0185	1·0079
14	1·0245	1·0200	1·0090
15	1·0262	1·0214	1·0101
16	1·0279	1·0228	1·0112
17	1·0295	1·0242	1·0123
18	1·0311	1·0256	1·0134
19	1·0327	1·0270	1·0144
20	1·0343	1·0284	1·0155
21	1·0359	1·0298	1·0166
22	1·0374	1·0311	1·0176
23	1·0390	1·0324	1·0187
24	1·0405	1·0337	1·0197
25	1·0420	1·0350	1·0207
26	1·0435	1·0363	1·0217
27	1·0450	1·0375	1·0227
28	1·0465	1·0388	1·0236
29	1·0479	1·0400	1·0246
30	1·0493	1·0412	1·0255
31	1·0507	1·0424	1·0264
32	1·0520	1·0436	1·0274
33	1·0534	1·0447	1·0283
34	1·0547	1·0459	1·0291
35	1·0560	1·0470	1·0300
36	1·0573	1·0481	1·0308
37	1·0585	1·0492	1·0316
38	1·0598	1·0502	1·0324
39	1·0610	1·0513	1·0332
40	1·0622	1·0523	1·0340
41	1·0634	1·0533	1·0348
42	1·0646	1·0543	1·0355
43	1·0657	1·0552	1·0363
44	1·0668	1·0562	1·0370
45	1·0679	1·0571	1·0377
46	1·0690	1·0580	1·0384
47	1·0700	1·0589	1·0391
48	1·0710	1·0598	1·0397
49	1·0720	1·0607	1·0404
50	1·0730	1·0615	1·0410
51	1·0740	1·0623	1·0416
52	1·0749	1·0631	1·0423
53	1·0758	1·0638	1·0429
54	1·0767	1·0646	1·0434
55	1·0775	1·0653	1·0440
56	1·0783	1·0660	1·0445
57	1·0791	1·0666	1·0450
58	1·0798	1·0673	1·0455
59	1·0806	1·0679	1·0460
60	1·0813	1·0685	1·0464
61	1·0820	1·0691	1·0468
62	1·0826	1·0697	1·0472
63	1·0832	1·0702	1·0475

$C_2H_4O_2$	Density		
p. c.	at 0°	at 15°	at 40°
64	1·0838	1·0707	1·0479
65	1·0845	1·0712	1·0482
66	1·0851	1·0717	1·0485
67	1·0856	1·0721	1·0488
68	1·0861	1·0725	1·0491
69	1·0866	1·0729	1·0493
70	1·0871	1·0733	1·0495
71	1·0875	1·0737	1·0497
72	1·0879	1·0740	1·0498
73	1·0883	1·0742	1·0499
74	1·0886	1·0744	1·0500
75	1·0888	1·0746	1·0501
76	1·0891	1·0747	1·0501
77	1·0893	1·0748	1·0501
78	1·0894	1·0748	1·0500
79	1·0896	1·0748	1·0499
80	1·0897	1·0748	1·0497
81	1·0897	1·0747	1·0495
82	1·0897	1·0746	1.0492
83	1·0896	1·0744	1·0489
84	1·0894	1·0742	1·0485
85	1.0892	1·0739	1·0481
86	1·0889	1·0736	1·0475
87	1·0885	1·0731	1·0469
88	1·0881	1·0726	1·0462
89	1·0876	1·0720	1·0455
90	1·0871	1·0713	1·0447
91	—	1·0705	1·0438
92	—	1·0696	1·0428
93	—	1·0686	1·0416
94	—	1·0674	1·0403
95	—	1·0660	1·0388
96	—	1·0644	1·0370
97	—	1·0625	1·0350
98	—	1·0604	1·0327
99	—	1·0580	1·0301
100	—	1·0553	1·0273

The maximum density corresponds at 0° to about 81 p.c., and at 40° to about 76 p.c. Ortho-acetic acid, $CH_3C(OH)_3$, would contain 77 p.c. of HOAc.

Reactions.—1. Vapour inflammable, burning with blue flame to water and CO_2.—2. Partly decomposed by passing through a red-hot tube yielding carbon and combustible gases, together with acetone, benzene, phenol, and naphthalene (Berthelot, *A. Ch.* [3] 33, 295).—3. Dropped upon hot $ZnCl_2$ it gives CO, CO_2, C_2H_4, C_3H_6, isobutylene, and a little CH_4 (Lebel a. Greene, *Am.* 2, 26).—4. Passed over *zinc dust* at 300°–350° it gives hydrogen, acetone, CO, and some propylene (Jahn, *M.* 1, 683).—5. Mixes with strong *sulphuric acid* without evolution of gas, but the mixture becomes hot, and if further heated gives off CO_2 mixed with SO_2. Dissolves SO_3 without giving off gas, forming sulpho-acetic acid. Not sensibly altered by *nitric acid*.—6. *Periodic acid* converts it into carbonic or formic acid, with formation of iodic acid and separation of iodine.—7. With *chlorine* in sunshine it forms mono- and tri-chloro-acetic acids (*q. v.*), the one or the other predominating according as the acetic acid or the chlorine is in excess.—8. Heated with *bromine* in a sealed tube it forms mono- and di-bromo-acetic acids. Not acted upon by *iodine*, even in sunshine.—9. With PCl_5 it forms AcCl, HCl, and $POCl_3$. With PCl_3 it reacts thus: $3AcOH + 2PCl_3 = 3AcCl + P_2O_3 + 3HCl$.—10. With P_2S_5 the products are thio-acetic acid and phosphoric oxide: $5AcOH + P_2S_5 = P_2O_5 + 5AcSH$.—11. With chromyl dichloride CrO_2Cl_2 it forms the compound $Cr_8O_7(C_2H_3O_2)_{10}8H_2O$ (Étard, *A. Ch.* [5] 22, 286).

Detection.—The solution supposed to contain acetic acid or an acetate is acidified with H_2SO_4 and distilled. The distillate, if acid, is neutralised with KOH and should then give the following tests: (1) $FeCl_3$ a brown-red colour, and a pp. on boiling. (2) $AgNO_3$ a white flocculent pp., sol. hot water, separating in spangles when the solution cools. (3) Evaporate to dryness, mix with As_2O_3 and heat: a disgusting odour of cacodyl is perceived.

Acetic Acid Dibromide $C_2H_4O_2.Br_2$ [37°] is formed on treating acetic acid with bromine in presence of a small quantity of carbon bisulphide. Orange-red needles or thick roseate prisms, very deliquescent; dissolving in water with great fall of temperature and separation of bromine, in alcohol, benzene, and glacial acetic acid with partial formation of substitution-products. At 100° dissociation first takes place, but finally HBr and $C_2H_3BrO_2$ are formed.

Compounds of acetic acid with Br and HBr. On adding bromine to well-cooled glacial acetic acid saturated with HBr, the whole solidifies to a mass of thick, rather large, tabular, crystals, which when dried have the composition $(C_2H_4O_2)_2Br_2HBr$; they fume in the air, melt and decompose at +8°, and are decomposed by water and by potash-lye, yielding $(C_2H_4O_2)_2.Br_2$ and $KBrO_3$. Heated in a sealed tube, they yield bromacetic acid (Steiner, *B.* 1874, 184). The compound $(C_2H_4O_2)_2Br_2.HBr$ has also been prepared by Hell a. Mühlhäuser (*B.* 1878, 241), who by using larger quantities of bromine have further obtained $(C_2H_4O_2)_4Br_6(BrH)_2$ in radiate groups of hard roseate crystals, which may be dried in the lime exsiccator.

Acetates.—Acetic acid is monobasic, the general formula of its normal salts being:

$$R^{(n)}(CH_3.COO)_n = R^{(n)}A'_n$$

the symbol $R^{(n)}$ denoting an *n*-valent radicle metallic or alkylic, and A′ standing for $C_2H_3O_2$.

METALLIC ACETATES.—The normal acetates all dissolve in water, and most of them readily. The least soluble are the silver and mercury salts, so that solutions of other acetates added to mercurous nitrate or silver nitrate throw down white shining scales of mercurous or silver acetate. But for the most part acetates are formed not by precipitation, but by the action of acetic acid on metallic oxides or carbonates; many carbonates, however, those of barium and calcium for example, are not decomposed by acetic acid in its most concentrated state. All acetates are decomposed by heat, most of them yielding carbon dioxide, acetone and an empyreumatic oil. Those which are easily decomposed, and likewise contain bases forming stable carbonates, are almost wholly resolved into acetone and carbonate, *e.g.*:

$$Ba(O.CO.Me)_2 = COMe_2 + BaCO_3.$$

Those which, like the potassium and sodium salts, require a higher temperature to decompose them, yield more complex products, but always a

certain quantity of acetone. Among the products are found methyl ethyl ketone and methyl propyl ketone, together with *dumasin* $C_6H_{10}O$ (Fittig, *A.* 110, 17). Acetates containing weaker bases give off part of the acetic acid undecomposed, the remaining portion being resolved into acetone and carbonic anhydride, or if the heat be strong, yielding empyreumatic oil and charcoal: the residue consists sometimes of oxide, sometimes, as in the case of copper and silver, of reduced metal; in this case part of the acetic acid is burnt by the oxygen abstracted from the metal. The decomposition of silver acetate may be expressed by the equation:

$$4CH_3.CO_2Ag = 3CH_3.CO_2H + CO_2 + C + 4Ag$$

(Iwig a. Hecht, *B.* 19, 238). Acetates heated with a large excess of fixed caustic alkali, are resolved at a temperature below redness into marsh gas and alkaline carbonate, *e.g.*:

$$KC_2H_3O_2 + KOH = K_2CO_3 + CH_4.$$

Acetates distilled with sulphuric acid and alcohol yield ethyl acetate. The acetates of the alkali-metals, and probably others also, treated with phosphorus oxychloride, yield acetyl chloride, together with a tribasic phosphate:

$$3NaOAc + POCl_3 = 3AcCl + Na_3PO_4.$$

Many acetates may be decomposed by water into acetic acid and metallic oxide. This decomposition in the case of aluminic and ferric acetates occurs at 100°, while at 175° the acetates of Mn, Co, Ni, Zn, Ur, Cu, and Ag, as well as ferrous and mercuric acetates, are slowly decomposed (Riban, *C. R.* 93, 1140).

Aluminium Acetates.—The *normal salt* AlA'_3 exists only in solution, being decomposed on evaporation. The solution, which is much used as a mordant in dyeing and calico-printing, and is called 'red liquor' because it yields madder reds and pinks, may be formed by dissolving freshly precipitated aluminium hydroxide in strong acetic acid, or by precipitating a solution of normal aluminium sulphate with lead acetate:

$$Al_2(SO_4)_3 + 3PbA'_2 = 3PbSO_4 + Al_2A'_6.$$

When quickly evaporated at a low temperature, by spreading it out in thin layers on glass or porcelain, it leaves a soluble basic acetate:

$$Al_2O_3.2C_4H_6O_3.4H_2O \text{ or } Al_2O(AcO)_4.4H_2O,$$

forming a gummy mass perfectly soluble in water; but, if heated, or left to evaporate at ord. temp., it deposits insoluble basic salts, containing in the first case two, and in the second five molecules of water, instead of four. The soluble acetate exposed in dilute solution to the temperature of boiling water for several days, undergoes a remarkable change, the whole or nearly the whole of the acid being expelled and a peculiar modification of alumina remaining dissolved (*v.* Aluminium) (Walter Crum, *C. J.* 6, 216). A dilute solution of aluminic acetate, free from alkali, may be boiled without a pp. being formed (Reinitzer, *M.* 3, 259).

Ammonium Acetates.—The normal salt NH_4A' [89°], obtained by saturating glacial acetic acid with dry ammonia-gas, is white, odourless, extremely soluble, and difficult to crystallise, its aqueous solution when evaporated giving off ammonia and leaving the acid salt (Berthelot, *Bl.* 22, 440; Smit, *Bl.* 24, 539; Bahrmann, *J. pr.* [2] 27, 296). When distilled with phosphoric anhydride it loses 2 mol. water, and gives off acetonitrile $C_2H_3N = NH_4C_2H_3O_2 - 2H_2O$. The aqueous solution known in the Pharmacopœia as *Spiritus Mindereri* is prepared by saturating aqueous acetic acid with ammonia or ammonium carbonate. The *acid salt* $NH_4HA'_2$ (145°) is obtained as a crystalline sublimate with evolution of ammonia by heating powdered ammonium chloride with potassium or calcium acetate (*v.* Acetamide). When commercial ammonium acetate is dissolved in its own weight of glacial acetic acid, an acid salt is obtained in long needles, having the composition $2NH_4A'3HA'$ (Berthelot, *Bl.* 24, 107).

Barium Acetate BaA'_2aq, prepared by decomposing the carbonate or sulphide with acetic acid, is obtained, on evaporating the solution at a gentle heat, in flattened prisms; and on cooling to 0°, in monoclinic prisms, $BaA'_2 3aq$. The crystals dried at 100° yield the anhydrous salt as a white powder, resolved at a high temperature into barium carbonate and acetone. S.G. (of BaA'_2aq) 2·02; (of BaA'_2) 2·47 (Schröder). V. e. sol. water, insol. alcohol.

Acid Salts.—$BaA'_2HA'2aq$.—$BaA'_2 2HA'2aq$. (Villiers, *Bl.* 30, 177; *C. R.* 85, 1234).

Double Salt.—$BaA'(NO_3)4aq$ (Lucius, *A.* 103, 113).

Bismuth Acetate separates in micaceous laminæ from a warm mixture of bismuth nitrate and potassium acetate. Acetic acid mixed with a solution of bismuth nitrate prevents the precipitation of that salt by water.

Cadmium Acetate $CdA'_2 3aq$. — Monoclinic prisms. V. e. sol. water, deliquescent and difficult to crystallise (Hauer, *Sitz. B.* 16, 131). S.G. 2·01 (dry, 2·34, Schröder).

Calcium Acetate CaA'_2aq. Small efflorescent needles. V. sol. water, sl. sol. alcohol. S.G. of aqueous solutions of CaA'_2 at 17·5° (Franz, *J. pr.* [2] 5, 298):

P.C.	S.G.	P.C.	S.G.	P.C.	S.G.
1	1·0066	11	1·0527	21	1·0925
3	1·0198	13	1·0597	23	1·1027
5	1·0330	15	1·0666	25	1·1130
7	1·0394	17	1·0750	27	1·1248
9	1·0458	19	1·0834	29	1·1366

Calcic acetate splits up on distillation into $CaCO_3$ and acetone.

Acid salt $CaA'_2HA'1\frac{1}{2}aq$. Hygroscopic.

Double salt $CaA'_2CaCl_2 10aq$. Monoclinic prisms, permanent in air.

Cerous Acetate $Ce_2A'_6 3aq$ forms radiate groups of small needles, which become anhydrous in dry air without losing their crystalline form; after drying at 115° they carbonise at a higher temperature without fusing, and when strongly heated leave a residue of cerous oxide (Lange, *J. pr.* 82, 129).

Chromium Acetates.—The *chromous salt*, CrA'_2aq, obtained from the chloride by decomposition with potassium or sodium acetate, forms red transparent crystals which when moist absorb oxygen very rapidly from the air, sometimes taking fire (Peligot, *A. Ch.* [3] 12, 541).—*Normal Chromic Acetate* $Cr_2A'_6 2aq$ is obtained by evaporating a solution of chromic hydroxide in acetic acid, as a green crystalline mass, insoluble in alcohol. Its aqueous solution, green by re-

flected, red by transmitted light, is not decomposed either by boiling or by addition of lime-water; but ammonia throws down from it a green precipitate of chromic hydroxide, soluble in excess (H. Schiff, *A. Ch.* [3] 71, 140; Schützenberger, *Bl.* [2] 4, 86). The solution of the normal acetate heated for several days with excess of chromic hydroxide loses its acid reaction, and yields by evaporation a green powder soluble in water, consisting of a basic acetate $Cr_2A'_4(OH)_2$ Schiff, *A.* 124, 168).

Chromic Diacetotetrachloride, $Cr_2A'_2Cl_4$ is obtained by dissolving Cr_2OCl_4 in strong acetic acid. It is an unstable salt, which gives off acetic acid when heated above 100°. The chlorine is but very slowly precipitated from it by silver nitrate at ordinary temperatures, but, on the other hand, the salt easily yields acetic ether when heated with sulphuric acid and alcohol (Schiff). — *Chromic Diaceto-sulphate* $Cr_2A'_2(SO_4)_2$, obtained by dissolving chromic disulphate in acetic acid, is a crystalline salt which becomes anhydrous at 100°, and gives off acetic acid at a higher temperature (Schiff).— *Chromic Pentaceto-nitrate* $Cr_2A'_5NO_3 4aq$ is obtained by mixing a solution of chromic hydroxide in a slight excess of acetic acid with a solution of the same quantity of chromic hydroxide in the exact quantity of nitric acid required to dissolve it. The concentrated solution, when left to itself, deposits an abundant crystallisation of a dark green salt, which may be purified by recrystallisation from water or from glacial acetic acid. It forms dark green bulky laminæ, which give off nitrous fumes at 100°, the chromium being at the same time converted into trioxide. (Schützenberger).

Cobalt Acetate $CoA'_2 4aq$.—Red needles.

Copper Acetates.—The *cuprous salt* $Cu_2A'_2$ sublimes towards the end of the distillation of normal cupric acetate. According to Berzelius, it is contained in green verdigris and sublimes on distillation. Soft loose white flakes which redden litmus and have a caustic astringent taste. Decomposed by water, yielding normal cupric acetate and cuprous oxide.

The *normal cupric salt* CuA'_2aq is prepared by dissolving cupric oxide or common verdigris in hot acetic acid, or by decomposing normal lead acetate with cupric sulphate. Dark-green monoclinic crystals (S.G. 1·9), efflorescent, soluble in 14 pts. cold and 5 pts. boiling water, sparingly also in alcohol, insoluble in ether. The solution boiled with grape-sugar yields a red precipitate of cuprous oxide. Cupric acetate crystallised at a temperature near 8° yields crystals containing $CuA'_2 5H_2O$. A solution of cupric acetate heated in a sealed tube at 200° forms crystallised cuprous oxide and cupric glycollate (Caseneuve, *C. R.* 89, 525).

Acid Cupric Acetate $CuA'_2HA'aq$ (Villiers, *C. R.* 85, 1234).

Basic Cupric Acetates.—These salts may be regarded as compounds of the normal salt with CuO, as compounds of Ac_2O with CuO, or, by taking account of water of crystallisation, as aceto-hydrates, *e.g.*:

Sesquibasic: $CuO.2CuA'_2.6aq =$
$3CuO.2Ac_2O.6Aq = 2CuA'(OH).CuA'_2.5aq$.

Dibasic: $CuO.CuA'_2 6Aq = 2CuO.Ac_2O.6aq = 2(HO.CuA')5aq$.

Tribasic: $2CuO.CuA'_2 2aq = 3CuO.Ac_2O.2aq = 2(HO.CuA')Cu(OH)_2$.

They are contained in *common verdigris* (*vert-de-gris*), a substance obtained by exposing plates of copper to the air in contact with acetic acid, and much used as a pigment and as a mordant in dyeing wool black. There are two varieties of this substance, the blue and the green, the former consisting almost wholly of dibasic cupric acetate, the latter of the sesquibasic salt mixed with smaller quantities of the dibasic and tribasic acetates. The *dibasic salt* or *blue verdigris* is prepared at Montpellier and in other parts of the south of France, by exposing copper to the air in contact with fermenting wine-lees. The same compound is obtained by exposing copper plates to damp air in contact with normal cupric acetate made into a paste with water. It forms delicate, silky, blue crystalline needles and scales, which yield a beautiful blue powder. They contain 6 mol. water, which they give off at 60°, and are then converted into a green mixture of the monobasic and tribasic salt.

Green Verdigris is manufactured at Grenoble by frequently sprinkling copper plates with vinegar in a warm room; and in Sweden by disposing copper plates in alternate layers with flannels soaked in vinegar.

Calcio-cupric Acetate $CaA'_2CuA'_2 8aq$, obtained by heating a mixture of 1 mol. CuA'_2 and 1 mol. $Ca(OH)_2$ with 8 pts. water and sufficient acetic acid to dissolve the precipitated CuO, and evaporating the filtrate at 25°–27°, crystallises in large blue square prisms, slightly efflorescent, giving off acetic acid and falling to powder at 75°; readily soluble in water. Another calcio-cupric acetate often exists in crystallised verdigris.

Cupric Aceto-arsenite $CuA'_2 3Cu(AsO_2)_2$.—*Schweinfurt green*, *Imperial green*, *Mitis green*, and when mixed with gypsum or heavy spar, *Neuwcider green*, *Mountain green*. Used as a pigment, and prepared on the large scale by mixing arsenious acid with cupric acetate and water. 5 pts. of verdigris are made up to a thin paste, and added to a boiling solution of 4 pts. or rather more of arsenious acid in 50 pts. of water. The boiling must be well kept up, otherwise the precipitate assumes a yellow-green colour, from formation of copper arsenite; in that case acetic acid must be added, and the boiling continued a few minutes longer. The precipitate then becomes crystalline, and acquires the fine green colour peculiar to the aceto-arsenite. The salt is insoluble in water, and when boiled with water for a considerable time, becomes brownish and gives up acetic acid. Acids abstract the whole of the copper, and aqueous alkalis first separate blue cupric hydroxide, which when boiled with the liquid is converted into cuprous oxide, an alkaline arsenate being formed at the same time.

Didymium Acetate $DiA'_3 4aq$. S.G. 1·882. S. V. S. 207·8.—DiA'_3aq. Red needles. S. G. 2·237. S.V.S. 150·6 (Clève, *Bl.* [2] 43, 365).

Erbium Acetate $EbA'_3 4aq$.—Isomorphous with didymium acetate (Thomsen, *B.* 6, 712).

Iron Acetates.—*Ferrous acetate* $FeA'_2 4aq$, obtained by dissolving iron or ferrous sulphide in strong acetic acid, separates on concentration in small colourless silky needles, which dissolve

readily in water and quickly absorb oxygen from the air.

Ferric Acetate is not known in the solid state as a salt of constant composition. The dark red solution of ferric hydroxide in acetic acid (*Liquor ferri acetici*) contains a basic salt. The following *basic ferric acetates* have been distinguished: $Fe_2A'_4(OH)_2$ obtained by dissolving at 50° the ferric hydroxide from 1 pt. Fe in 10 pts. acetic acid of 30 p.c. and evaporating at 70°. Amorphous, soluble in alcohol and water (Oudemans, *J.* 1858, p. 282).—$Fe_2A'_3(OH)_3$, probably contained in the red solution formed on treating $Fe_2A'_3(OH)Cl_2$ (*infra*) with silver oxide. Becomes syrupy in a vacuum but does not crystallise; decomposes quickly at ord. temp., forming an ochreous jelly (Scheurer-Kestner).—$Fe_2A'_2(OH)_4 2Fe_2O_3$ is the ochreous deposit formed in a solution of ferrous acetate exposed to the air. Other basic salts appear to be formed in the decomposition of the normal salt by heat or otherwise. A solution of ferric acetate, quite free from other salts, is not ppd. by boiling (Reinitzer, *M.* 3, 257).

Acetonitrates (Kestner, *A. Ch.* [3] 63, 422; 68, 472; *J.* 1861, 307).—Formed by mixing solutions of ferric nitrate and acetate in various proportions, or by dissolving ferric hydroxide in various mixtures of acetic and nitric acids. Mostly very unstable, decomposed by boiling with water.—$FeA'_3(OH)_2NO_3$ forms deep red flattened prisms, very soluble in water and in alcohol, insol. in ether.—$FeA'_4(OH)NO_3 4aq$ forms red-brown rhombic prisms, sol. in water and alcohol, decomposing on slight rise in temperature. The *diformi-diaceto-nitrate* $Fe_2(COH)_2(OAc)_2(NO_3)_2$ is very soluble in water and alcohol, insol. in ether, very unstable.

Acetochlorides — $Fe_2A'_3Cl_2(OH)3aq$ is obtained on cautiously adding nitric acid to a solution of $FeCl_2$ in acetic acid at 86°; also when ferric hydroxide (1 mol.), acetic acid (1 mol.), and hydrochloric acid (1 mol.) are digested together at 40° for two or three days. Very hard crystals, black by reflected, red by transmitted light, very soluble in water. With silver oxide they yield ferric triacetate (K.; Schiff, *A. Ch.* [3] 66, 136).—$Fe_2A'_4Cl_2$, obtained by dissolving 1 mol. ferric hydroxide in a mixture of HCl (2 mol.) and $C_2H_4O_2$ (4 mols.), or by oxidising ferrous chloride dissolved in very strong acetic acid with nitric acid. Yellowish-red crystals, sol. in water and in alcohol, easily resolved into acetic acid and $Fe_2A'_3(OH)Cl_2$. Heated at 50° for twelve hours with silver nitrate, it is converted into *ferric tetraceto-dinitrate*:

$$Fe_2A'_4Cl_2 + 2AgNO_3 = 2AgCl + Fe_2A'_4(NO_3)_2.$$

Lanthanum Acetate $LaA'_3 1\frac{1}{2}aq.$ — Small needles (Clève, *Bl.* [2] 21, 196).

Lead Acetates, or *Plumbic Acetates.*—The *normal salt* $PbA'_2 3aq$, *Sugar of lead, Sel saccharum Saturni*, [75°] S.G. 2·5.—Prepared by dissolving lead oxide or carbonate in acetic acid (Wichmann, *J.* 1853, 738).

Properties.—Monoclinic efflorescent crystals, easily soluble in water and in spirit of ordinary strength, insoluble in cold absolute alcohol, completely dehydrated by prolonged boiling with absolute alcohol. An aqueous solution saturated at 15° contains 387·623g. salt in a litre, and has a density of 1·2367 (Michel a. Kraft, *J.* 1854, p. 296).

Density of the Aqueous Solution at 14°. (Oudemans, *Fr.* 7, 419; *J.* 1868, 29.)

Cryst.Salt p.c.	Density	Cryst.Salt p.c.	Density
1	1·0057	20	1·1399
5	1·0317	25	1·1808
10	1·0659	30	1·2248
15	1·1018	33	1·2525

Normal lead acetate melts at 75°, begins to give off water with a portion of its acid a little above 100°, and is completely dehydrated at 280°. Above that temperature it decomposes, giving off acetic acid, carbonic anhydride, and acetone, and leaving metallic lead very finely divided and highly combustible. The aqueous solution is partially decomposed by the carbonic acid of the air, carbonate of lead being precipitated, and a portion of acetic acid set free, which prevents further decomposition. The solution is not precipitated by ammonia in the cold, but yields crystals of lead oxide when heated with a large excess of ammonia. Normal lead acetate forms crystalline compounds with chloride and peroxide of lead (*Gm.* 8, 310). Bromine added to a solution of the normal salt throws down a brown precipitate of PbO_2, which, if the liquid be warmed, continues to form till 2 at. Br have been added to 2 mol. PbA'_2. The solution then contains lead bromide and acetic acid:

$$2PbA'_2 + 2H_2O + Br_2 = PbO_2 + PbBr_2 + 4HA'$$

(Chapman a. Smith, *C. J.* 22, 185).

Basic Lead Acetates. — $Pb_2A'_3(OH)$, formed by repeatedly drenching the normal salt with absolute alcohol; the residue crystallises from hot absolute alcohol in nacreous six-sided plates, easily soluble in water, sparingly in cold alcohol (Plöchl. *B.* 13, 1647).—$PbA'_2PbO 2aq$. *Lead-vinegar, Acetum Saturni.* Prepared by dissolving litharge in the aqueous normal salt, and evaporating at a gentle heat, whereupon it crystallises in needles. According to Wittstein (*A.* 52, 253) the crystals contain only 1 mol. H_2O. Easily soluble in water and in alcohol of 90 p.c. Reacts alkaline. Decomposed by CO_2. A solution of this salt mixed with alcohol forms *Goulard's lotion.*—$PbA'_2 2PbOaq$, obtained by dissolving PbO in normal lead acetate, or by mixing a solution of the normal salt with ammonia. Crystallises in silky needles, soluble in 5·55 pts. water at 100°, insoluble in absolute alcohol (Payen, *A.* 25, 124; *A. Ch.* [4] 8, 6; Löwe, *J. pr.* 98, 385; *J.* 1866, 235).

An *Aceto-chloride* $ClPbA'$ is formed by heating recently precipitated lead chloride with normal lead acetate and acetic acid at 160°, and crystallises in monoclinic prisms. Decomposed by water into lead chloride and the more soluble salt PbA'_2ClPbA'. The analogous compounds, $BrPbA'$ and $IPbA'$ obtained in like manner, form small monoclinic crystals (Carius, *A.* 125, 87).

Sodio- and *Potassio-plumbic Acetates.*—$PbA'_2NaA'\frac{3}{2}aq$. Monoclinic crystals (Rammelsberg, *J.* 1855, 503).—$PbA'_2 2PbO 4KA'$ is formed on adding potash-lye (S.G. 1·06) with agitation to a boiling solution of normal lead acetate (S.G. 1·25 to 1·30). Crystalline pulp, moderately soluble in water (Taddei, *J.* 1847–8, 548).

Aceto-formate $(CHO_2)Pb_2(C_2H_3O_2)_3 2aq.$

Needles, easily soluble in water, sparingly in alcohol (Plöchl. *B.* 13, 1645).

Lithium Acetates. — $LiA'2aq$. Rhombic prisms [c. 70°]. Dissolves in less than $\frac{1}{3}$ pt. water at 15°; in 4·64 pts. alcohol of density 0·81 at 14° (Fleisch. *Zeitschr. f. Physik*, 4, 108). According to Rammelsberg (*A.* 56, 221), the crystals contain only 1 mol. H_2O.—$LiA'HA'$, obtained by spontaneous evaporation of a solution of the normal salt in glacial acetic acid [99°]. Rotates on water. Under somewhat different circumstances it crystallises in small four-sided plates, containing Aq and melting at 85° (Lescœur, *Bl.* 24, 516).

Magnesium Acetate $MgA'_2 4aq$. — S.G. 1·45 (Schröder). Monoclinic, slightly deliquescent, very soluble in water and in alcohol (v. Hauer, *J.* 1855, 501; Patrouillard, *C. R.* 84, 553).

Manganous Acetate $MnA'_2 4aq$. — Pale red transparent monoclinic plates, permanent in the air, soluble in 3-3·5 pts. water, also in alcohol. S.G. 1·6 (Schröder).

Acid Salt $MnA'_2 HA'2aq$ (Villiers, *Bl.* 30, 177).

Manganic Acetate $MnA'_3 2aq$.—Brown crystals (Otto, *A.* 93, 372; Christensen, *J. pr.* [2] 28, 14).

Mercury Acetates.—1. $Hg_2A'_2$. Obtained by precipitation. Micaceous scales. S. ·75 at 13°. —HgA'_2. Brilliant micaceous laminæ. S. 25 at 10°, 36 at 19°, 100 at 100°. Dissolves with partial decomposition in 17·7 pts. alcohol (S.G. ·811) at 19° (*Gm.* 8, 332).—An *aceto-sulphide*, $HgA'_2 HgS$, is precipitated, on passing H_2S into a solution of mercuric acetate, as a white crystalline powder.—*Mercuro-diammonium Acetate* $N_2H_6HgA'_2H_2O$. Rectangular plates; easily soluble in water, nearly insoluble in alcohol; smells of acetic acid, and decomposes gradually on exposure to the air (Hirzel, *J.* 1851, 437).

Nickel Acetate.—Apple-green prisms, soluble in 6 pts. cold water, insoluble in alcohol (Tupputi, *A. Ch.* 78, 164).

Potassium Acetates. — *Normal salt* KA'. *Terra foliata tartari.*—S. 188 at 2°; 229 at 13·9°; 492 at 62° (Osann). A boiling saturated solution contains 8 pts. salt to 1 pt. water, and boils at 169° (Berzelius). Soluble in 3 pts. cold and 2 pts. hot alcohol. Exists in many plant-juices. White, difficult to crystallise, extremely deliquescent, insoluble in ether. Chlorine passed into its aqueous solution liberates CO_2 and forms a bleaching liquid. On passing an electric current through a concentrated aqueous solution of the salt, hydrogen is evolved at the negative pole, and at the positive a mixture of ethane and CO_2. The principal decomposition is: $2(CH_3.CO_2H) = C_2H_6 + 2CO_2 + H_2$, methyl oxide and acetate being secondary products (Kolbe, *A.* 69, 257). On passing CO_2-gas into a solution of the salt in alcohol of 97-100 p.c., a large quantity of potassium carbonate is thrown down, and ethyl acetate is formed (Pelouze, *A.* 5, 265).

Acid Potassium Acetate KA'HA' is formed when the normal acetate is evaporated with an excess of strong acetic acid, and separates in needles or laminæ, or in long flattened prisms. Very deliquescent; melts at 148°, and decomposes at 200°, giving off pure AcOH. This affords an easy method of obtaining glacial acetic acid. Acid potassium acetate is also formed when the normal salt is distilled with butyric or valeric acid; but neither of these acids decomposes the salt thus produced. Hence when butyric or valeric acid is mixed with acetic acid, a separation more or less complete may be effected by half neutralising the liquid with potash and distilling. If the acetic acid is in excess, acid potassium acetate alone remains behind, the whole of the butyric or valeric acid passing over, together with the remainder of the acetic acid. If, on the contrary, the other acid is in excess, it passes over unmixed with acetic acid, and the residue consists of potassium acetate mixed with butyrate or valerate. By repeating the process a certain number of times either on the acid distillate or on the acid separated from the residue by distillation with sulphuric acid, complete separation may be effected. Acetic acid, therefore, is an exception to the rule that when a mixture of fatty acids and their potassium salts is boiled the most volatile acids distil over (Liebig, *A.* 71, 355).—KA'2HA' [112°]. S.G. 1·4. Deliquescent plates (Lescœur, *Bl.* 22, 156).

Anhydrous Potassium Diacetate or *Potassium Pyroacetate* $K_2C_8H_{12}O_7 = 2KOAc.Ac_2O$, prepared by dissolving melted KOAc in boiling acetic anhydride, forms colourless needles very soluble in water, less deliquescent than normal potassium acetate. Decomposed by heat, giving off Ac_2O (Gerhardt, *A. Ch.* [3] 37, 317).

Rhodium Acetate $RhA'_3 2\frac{1}{2}aq$ (Claus, *J.* 1860, 213).

Rubidium Acetate RbA'.—Plates (Grandeau, *J.* 1863, 184).

Samarium Acetate $SmA'_3 4aq$.—S.G. 1·94. S.V.S. 205·6. Yellow crystals (Clève, *Bl.* [2] 43, 171).

Silver Acetate AgA' (S. 1·02 at 14°) separates on mixing the concentrated solutions of $AgNO_3$ and NaOAc. Dissolves in hot water, and on cooling separates as nacreous flexible laminæ. Heated with *iodine* it is resolved into silver iodide, methyl acetate, hydrogen acetate, CO_2, acetylene, and hydrogen (Birnbaum, *A.* 152, 111). When dry, it combines with NH_3, forming $AgA'2NH_3$ (Reychler, *B.* 17, 47).

Sodium Acetates. — NaA'3aq. [58°] (123°). S.G. 1·4. S. 26 at 6°, 42 at 37°, 59 at 48° (Osann). S. (alcohol of S.G. ·8322) 2·1 at 18°. Crystallises with $3H_2O$ in monoclinic prisms, melting below 100°. According to Reischauer (*J.* 1860, 50), the crystals give off the whole of their water in a vacuum at ord. temp. The fused salt in damp air quickly takes up about $7H_2O$, forming a supersaturated solution, whereas the unfused salt takes up from the air only the original $3H_2O$. When the aqueous solution of NaA' turns mouldy, oxygen is absorbed, and small quantities of alcohol and formic acid are produced (Béchamp, *Z.* 6, 438).

The S.G. of solutions containing the following percentages of NaA' is given by Franz (*J. pr.* [2] 5, 297) as follows:

P.C.	S.G.	P.C.	S.G.	P.C.	S.G.
1	1·0058	11	1·0591	21	1·1134
3	1·0174	13	1·0697	23	1·1254
5	1·0292	15	1·0802	25	1·1374
7	1·0390	17	1·0910	27	1·1506
9	1·0488	19	1·1018	29	1·1638

The S.G. of a saturated solution being 1·1842.

Acid Sodium Acetates (Villiers, *Bl.* 29, 153; 30, 175; *C. R.* 85, 1234; Lescœur, *Bl.* 22, 156).—NaA'HA'aq. Cubic (Fehling).—NaA'2HA' or NaA'2HA'aq. Long needles. [127°]—
5NaA'4HA'6aq.—4NaA'HA'11aq.—
5NaA'2HA'18aq.
The three last are, perhaps, mixtures.

Strontium Acetates SrA'_2 ½aq.—Below 15° it crystallises with 4Aq in monoclinic prisms.

An *aceto-nitrate* $NO_3SrA'\frac{3}{2}H_2O$ forms triclinic crystals (Hauer, *J.* 1858, 281; Zepharovich, *J.* 1860, 309). Villiers (*Bl.* 30, 176) describes the following acid acetates:
$SrA'_2HA'2aq$. $3SrA'_24HA'6aq$. $2SrA'_23HA'1\frac{1}{2}aq$.

Thallium Acetates.—*Thallous acetate* TlA'. White silky needles, easily soluble in water and in alcohol, and deliquescent (Crookes, *C. J.* 27, 149).

Acid Salt TlA'HA' [64°] (Lescœur, *Bl.* 24, 516).

Basic Thallic Acetate $TlA'_32Tl(OH)_3$ 1½aq. Colourless plates, readily resolved into acetic acid and thallic oxide.

Tin Acetates.—Tin dissolves slowly in boiling acetic acid, with evolution of hydrogen, and stannous hydroxide dissolves readily in the boiling acid, the solution when evaporated to a syrup and covered with alcohol yielding small colourless crystals. Stannic hydroxide also dissolves in the acid, the solution when evaporated leaving a gummy mass. Stannic chloride forms a crystalline compound with glacial acetic acid.

Uranium Acetates.—*Uranous acetate.* Warty groups of green needles.—*Uranic acetate* or *Uranyl acetate* $UO_2A'_2$, obtained by heating uranic nitrate till it begins to give off oxygen, dissolving the yellowish-red mass, which still contains NO_3H, in warm concentrated acetic acid, and evaporating to the crystallising point. Crystallises from strongly acid solutions in yellow transparent monoclinic prisms, containing $UO_2A'_22aq$, which dissolve in boiling water with separation of UO_3, but are reproduced on evaporating the solution. A weaker solution cooled below 10° deposits quadratic octahedrons of $UO_2A'_23aq$, which give off 1 mol. H_2O at 200°, the rest at 275°. *Double Salts.*—$NH_4A'UO_2A'_23aq$, $NaA'UO_2A'_2$ (regular tetrahedrons), and $KA'UO_2A'_2aq$ (quadratic prisms), are obtained by adding the respective alkaline carbonates to a solution of uranic acetate till a precipitate is formed consisting of alkali-metal uranate, redissolving this in a slight excess of acetic acid, and cooling to crystallisation. The other double salts of the group are formed by boiling the carbonates with uranic acetate till all the UO_3 is precipitated, redissolving in acetic acid and evaporating.—$BaA'_22UO_2A'_26aq$. Small yellow crystalline spangles, easily soluble in water; give off their crystal-water at 275° (Wertheim, *J. pr.* 29, 227).—$CaA'_22UO_2A'_28aq$. Sulphur-yellow rhombic crystals, easily soluble in water, permanent in the air, becoming anhydrous at 200° (Weselsky, *J. pr.* 75, 55).—$CdA'_22UO_2A'_26aq$. Dichroic crystals.—$PbA'_2UO_2A'_2$ 6aq. Tufts of pale yellow needles.—$MgA'_22UO_2A'_2$ 8aq. Rectangular prisms.—$NiA'_22UO_2A'_2$ 7aq. Emerald-green rhombic crystals.—$SrA'_2UO_2A'_2$ 6aq. Sulphur-yellow crystals.—$ZnA'_22UO_2A'_2$ 8aq. Sulphur-yellow crystals, isomorphous with the nickel salt.

$MnA'_2UO_2A'_2$ 6aq. $FeA'_2UO_2A'_2$ 7aq.
$TlA'2UO_2A'_2$ 2aq. $LiA'UO_2A'_2$ 3aq.
$BeA'_2UO_2A'_2$ 2aq. $AgA'UO_2A'_2$ aq.

Zinc Acetate.—ZnA'_2 3aq. [235°-257°] S.G. 1·72.—ZnA'_2 [242°] S.G. 1·84.—Monoclinic laminæ. Very soluble in water. May be sublimed as ZnA'_2, especially *in vacuo* (Franchimont, *B.* 12, 11). ZnA'_2 may be crystallised, in anhydrous state, from HOAc (Peter a. Rochefontaine, *Bl.* [2] 42, 573).

Yttrium Acetate YA'_3 8aq(?).—Isomorphous with the acetates of didymium and erbium (Clève).

ALKYL ACETATES. *Acetic Ethers.*

Methyl Acetate $C_3H_6O_2$ or MeA'. M.w. 74 (55°) at 754·4 mm. (R. Schiff); (56·3°) at 760 mm (Kopp); (57·3°) (Gartenmeister); (57·5°) at 760 mm. (Elsässer, Perkin). S.G. $\frac{0}{0}$ ·9643 (G.) $\frac{0}{4}$ ·9577 (E.); $\frac{15}{15}$ ·9398 (P.); $\frac{20}{4}$ ·9039 (Brühl); $\frac{25}{25}$ ·9286 (P.); $\frac{65}{}$ ·8825 (S.). V.D. 2·563 (for 2·564). C.E. (0°-10°) ·00133 (G.); ·00136 (E.). S. 33 at 22° (J. Traube). S.V. 83·66 (S.); 83·2 (G.); 83·77 (E.). μ_β 1·3654. R_∞ 28·78 (B.). H.F.p. 96,720. H.F.v. 94,980. M.M. 3·362 at 22° (P.).

Occurrence.—In crude wood-vinegar (Weidmann a. Schweizer, *P.* 43, 593).

Preparation.—1. By distilling 2 pts. wood-spirits with 1 pt. very strong acetic acid and 1 pt. strong sulphuric acid, removing the excess of wood-spirit by means of fused calcium chloride, and rectifying over sodium carbonate (Dumas a. Peligot [1835], *A. Ch.* [2] 58, 46). 2. By heating H_2SO_4 (50 c.c.) and MeOH (50 c.c.) to 140° and running in slowly a mixture of equal parts of MeOH and HOAc (Pabst, *Bl.* [2] 33, 350). 3. By distilling 3 pts. wood-spirit with 14·5 pts. dried lead acetate and 5 pts. strong sulphuric acid, agitating the distillate with milk of lime, treating the supernatant oil with calcium chloride, and rectifying (Kopp, *A.* 55, 181).

Properties. — Colourless fragrant liquid. Soluble in water; mixes in all proportions with alcohol and ether.

Reactions.—1. Aqueous solution only slightly decomposed by boiling.—2. Resolved by caustic *alkalis* into methyl alcohol and acetic acid.—3. When poured on pulverised *soda-lime* it is violently decomposed, with formation of sodium acetate and formate, and evolution of hydrogen.—4. With *sodium* it reacts like ethyl acetate (*q. v.*), yielding as chief products sodium methylate, $NaOCH_3$, and methyl sodio-aceto-acetate, COMe.CHNa.COOMe.—5. Decomposed by strong sulphuric acid, becoming hot, giving off acetic acid, and forming methyl sulphuric acid.

Chloro-methyl Acetate CH_2ClOAc (115° i.V.). S.G. $\frac{14.5}{}$ 1·195. V.D. 3·70 (for 3·74).—Made by passing chlorine into methyl acetate at 10°. An oil. Slowly decomposed by water, quickly by alkalis, giving HCl, HOAc, and formic aldehyde:

$$CH_2Cl(OAc) + 2KOH = CH_2O + H_2O + KCl + KOAc.$$

With alcoholic KOAc it gives methylene acetate, $CH_2(OAc)_2$ *v.* formic aldehyde (L. Henry, *B.* 6, 740).

Di-chloro-methyl Acetate $CHCl_2.OAc$ (145°-148°), S.G. 1·25, is formed by passing dry chlorine through methyl acetate at a gentle heat. Colourless, pungent-smelling liquid. Decomposed slowly by water, quickly by aqueous potash,

violently by alcoholic potash, yielding formic, acetic, and hydrochloric acids,

$$CHCl_2(OAc) + 5KOH =$$
$$CH_2(OK)O + H_2O + 2KCl + KOAc$$

(Malaguti, *A.* 32, 47).

Tri-chlorinated Methyl Acetate $C_3H_3Cl_3O_2$ (145°). Laurent, *A. Ch.* [2] 73, 25.

Per-chlorinated Methyl Acetate $CCl_3.O.CO.CCl_3$. Formed by prolonged action of Cl on methyl acetate *v. tri*-CHLORO-ACETIC ACID.

Ethyl Acetate $C_4H_8O_2$ or EtA'.—*Acetic ether.* M.w. 88. (75·5°–76·5°) at 745·5 mm. (R. Schiff); (77·1°) at 760 mm. (Elsässer); (77·5°) (Gartenmeister). S.G. $\frac{0}{0}$ ·9253 (G.); $\frac{0}{4}$ ·9239 (E.); $\frac{20}{4}$ ·9007 (Brühl); $\frac{15}{15}$ ·9072, $\frac{25}{25}$ ·8971 (Perkin); $\frac{77.5}{4}$ ·8306 (S.) V.D. 3·087 (for 3·079). S.H. ·48. C.E. (0°–10°) ·001263 (E.). S. 6 at 17·5°. S.V. 105·7 (S.); 106·1 (G.); 106·15 (E.). μ_β 1·3771. R_∞ 35·46 (B.). H.F.p. 114,710. H.F.v. 112,290.

Formation.—(Lauragais, *J. d. Sçavans*, 1759, 324; Thenard, *Mém. d'Arcueil*, 1, 153; Dumas a. Boullay, *J. Ph.* 14, 113; Liebig, *A.* 5, 34; 30, 144; Malaguti, *A. Ch.* [2] 20, 367; [3] 162, 58).

1. By heating alcohol with acetic acid or with an acetate and strong sulphuric acid. 2. By distilling calcium or potassium ethyl-sulphate with glacial acetic acid (Liebig).

Preparation.—1. By distilling a mixture of 3 pts. potassium acetate, 3 pts. absolute alcohol, and 2 pts. sulphuric acid; or 10 pts. sodium acetate, 6 pts. alcohol, and 15 pts. sulphuric acid; or 16 pts. dry lead acetate, $4\frac{1}{2}$ pts. alcohol, and 6 pts. sulphuric acid. The acid is first mixed with the alcohol, and the liquid is poured upon the pulverised salt; the mixture is then distilled to dryness, and the product is purified by digestion with calcium chloride and rectification.—2. Frankland a. Duppa prepare ethyl acetate by gradually pouring a mixture of 3·6 kilo. of 97-p.c. alcohol, and 9 kilo. strong sulphuric acid, on 6 kilo. sodium acetate previously fused and dried, leaving the mixture at rest for 12 hours, then distilling and rectifying the distillate (which is free from alcohol and amounts to 6 kilo.) over fused and pulverised calcium chloride. The best mode of mixing the alcohol and sulphuric acid is to pour the alcohol through a narrow glass tube to the bottom of the vessel containing the acid, stirring the liquid continually by means of the tube. It is best to leave the ethyl-sulphuric acid thus formed for 24 hours before pouring it on the sodium acetate. 3. A mixture of alcohol and acetic acid in molecular proportions is allowed to run into sulphuric acid at 130°, whereby ethyl-sulphuric acid is first formed, and this with the acetic acid forms ethyl acetate, which distils over, leaving the sulphuric acid to be further acted on by the alcohol. By this process 10 g. sulphuric acid yield 232 g. ethyl acetate (Eghis, *B.* 6, 1177; Pabst, *Bl.* [2] 33, 350).

Properties.—Colourless fragrant liquid. Soluble in 17 pts. water at ord. temp.; dissolves ·036 pts. of water, freely miscible with alcohol and ether.

Reactions.—1. *Burns* with yellowish flame. 2. By dilute *chromic acid* it is oxidised to acetic acid $C_4H_8O_2 + O_2 = 2C_2H_4O_2$ (Chapman a. Thorp, *C. J.* 19, 484).—3. Permanent in the *air* when dry, but gradually decomposing when moist into alcohol and acetic acid; more quickly in contact with alkalis.—4. Converted by heating with *sulphuric acid* into ethyl oxide and acetic acid; with *hydrochloric acid* into acetic acid and ethyl chloride.—5. The vapour passed over *zinc-dust* at 300°–350° gives acetone, CO, hydrogen and ethylene (Jahn, *B.* 13, 2107).—6. With *lime* in sealed tubes at 250°–280° it yields butyric acid as chief product, calcium acetate and ethylate as intermediate products:

$$2CaO + 2EtOAc = Ca(OAc)_2 + Ca(OEt)_2 =$$
$$Ca(OH)_2 + Ca(C_4H_7O_2)_2$$

(Lubavin, *Bl.* [2] 34, 679).—7. With *alkaline hydroxides* it yields acetic acid and ethyl alcohol; with the *anhydrous oxides*, acetic acid and a metallic ethylate:

$$2EtOAc + Ba(OH)_2 = Ba(OAc)_2 + 2EtOH; \text{ and}$$
$$2EtOAc + 2BaO = Ba(OAc)_2 + Ba(OEt)_2$$

(Berthelot a. Fleurieu, *A. Ch.* [3] 17, 80).—8. With a mixture of *lime-water* and *chloride of lime* (bleaching powder), it yields chloroform (Schlagdenhauffen, *J. Ph.* [3] 36, 190).—9. With alcoholic KHS it forms, on heating, KOAc and H_2S, but no mercaptan (C. Gottig, *J. pr.* [2] 33, 90).—10. With *sodium-ethylate*, forms, at 130°, sodio-aceto-acetic ether.—11. Ethyl acetate heated with *sodium* dissolves the metal, and the whole solidifies to a crystalline mass of sodium ethylate and ethyl sodio-aceto-acetate $C_6H_9NaO_3$. The reaction is either

$$2(C_2H_5.O.Ac) + Na_2 = NaOC_2H_5 + C_6H_9NaO_3 + H_2;$$
$$\text{or } 3(C_2H_5.O.Ac) + Na_4 = 3NaOC_2H_5 + C_6H_9NaO_3.$$

The quantity of hydrogen evolved varies considerably according to the temperature and pressure at which the reaction takes place, and the proportions of the materials used; sometimes no gas is evolved (equ. 2), and under no circumstances yet observed is the quantity of hydrogen evolved exactly equivalent to the sodium dissolved, as required by the first equation. Probably, therefore, the two reactions generally take place together (see, further, ACETO-ACETIC ACID).—12. With *iodine* and *aluminium foil* ethyl acetate yields ethyl iodide and aluminium acetate, $6EtOAc + Al_2 + 3I_2 = 6EtI + Al_2(OAc)_6$, and a similar reaction takes place with all the alkyl acetates of the series $C_nH_{2n+1}OAc$ (Gladstone a. Tribe, *C. J.* 30, 357).—13. Ethyl acetate combines with titanic chloride in various proportions (Demarçay, *Bl.* [2] 20, 127; *C.R.* 70, 1414).

CHLORINATED ETHYL ACETATES.—Chlorine is abundantly absorbed by ethyl acetate, and acts strongly upon it, even at ordinary temperatures, replacing two or more atoms of hydrogen; the action is accelerated by heat and by direct sunshine. Seven compounds have been described as thus formed, containing 2 to 8 at. chlorine in place of hydrogen, but only three of them have been obtained of constant composition, viz., those containing 2, 3, and 5 at. chlorine.

Dichlorethyl Acetate $C_4H_6Cl_2O_2$ *i.e.* $C_2H_3Cl_2.C_2H_3O_2$ is the product formed when ethyl acetate is kept cool and in the shade during the action of the chlorine. Transparent oil. S.G. 3·01 at 12° (Malaguti, *A. Ch.* [2] 70, 367).

Trichloro-ethyl-acetate $CHCl_2.CHCl.OAc$, metameric with *ethyl tri*-CHLORO-ACETATE (*q.v.*) is formed by the action of chlorine at 120°, in presence of iodine, on ethylidene aceto-chloride, $CH_3CHCl.OAc$ (Kessel, *B.* 10, 1999).

—$CCl_3.CH_2OAc$ (72°) at 18mm., (167°) at 736mm. S.G. $\frac{22}{}$ 1·39; V.D. 6·89 (for 6·63). From trichloro-ethyl alcohol and AcCl at 130°. Rectified

in vacuo (Garzarolli-Thurnlackh, *A.* 210, 63). Fuming HNO_3 converts it, at 15°, into tri-chloro-acetic acid. KOH forms tri-chloro-ethyl-glycollic acid, $CCl_3.CH_2.O.CH_2CO_2H$.

Octo-chlorinated Ethyl Acetate $C_4Cl_8O_2$ *i.e.* $C_2Cl_5.C_2Cl_3O_2$ is slowly formed on exposing the dichlorinated ether, together with chlorine, at 100° to bright summer sunshine. The product, after distillation in a stream of carbon dioxide to remove excess of chlorine, forms a colourless pungent oil which remains liquid below 0°. S.G. 1·79 at 25°. Boils, with partial decomposition, at 245°. Its vapour passed over fragments of glass heated to 400° is converted into the isomeric compound chloraldehyde $C_2Cl_4O = CCl_3.COCl$. It is decomposed by water and moist air, and more completely by KOH, into hydrochloric and trichloracetic acids:

$$C_2Cl_5.C_2Cl_3O_2 + 2H_2O = 2HCl + 2(CCl_3.CO_2H)$$

(Leblanc, *A. Ch.* [3] 10, 197; Malaguti, *ib.* 15, 258).

The following chlorinated acetic ethers are also known: the compound of ALDEHYDE with AcCl, GLYCOL chloro-acetin, and the ethyl salts of the three CHLORO-ACETIC ACIDS.

BROMINATED ETHYL ACETATES $C_4H_6Br_2O_2 = CH_2Br.CO.OCHBr.CH_3$ (bromethyl bromacetate), formed on heating ethylidene acetate-chloride $CHMeCl(OAc)$ with bromine at 100°–103°, boils under reduced pressure at 130–135°, and dissolves in boiling water, with formation of aldehyde, acetic acid, crotonaldehyde, acetal, ethyl bromide, and HBr. The crotonaldehyde and acetal are secondary products formed from acetaldehyde, produced in the first instance as shown by the equations:

$$CH_2Br.CO.OCHBr.CH_3 + C_2H_5OH =$$
$$CH_2Br.COOC_2H_5 + CH_3.CHBr(OH)$$
$$\text{and } CH_3.CHBr(OH) = HBr + CH_3.CHO.$$

Tri- and Tetra-brominated Ethyl Acetates $C_4H_5Br_3O_2$ and $C_4H_4Br_4O_2$, formed by the action of 1 or 2 mol. bromine at 120° and 160°, respectively, on $C_4H_6Br_2O_2$, and freed from absorbed HBr by heating in a stream of carbon dioxide, are oily strongly fuming liquids, partly decomposing on distillation; decomposed also by water and alcohol, the products containing substances which reduce ammoniacal silver solution, whence it appears that both these ethers produce aldehydes. The *pentabrominated* compound $C_4H_3Br_5O_2$, probably $CH_2Br.CO.OCBr_2.CHBr_2$, formed by heating $C_4H_4Br_4O_2$ with 1 mol. bromine at 170°, is a liquid which scarcely fumes in the air (176°). Its product of decomposition by water does not reduce ammoniacal silver solution. Heated with excess of bromine, it forms $C_4H_2Br_6O_2$ (195°–198°) (Kessel, *B.* 10, 1994; 11, 1917). Other brominated acetic ethers are $CH_3CHBr.OAc$ *v.* ALDEHYDE, $CH_2Br.CH_2.OAc$ *v.* GLYCOL, and the ethylic BROMO-ACETATES.

Ethyl Ortho-acetate $CH_3.C(OEt)_3$.—Triethylic acetate; (142°), S.G. $\frac{22}{}$ ·94, formed, together with $CH_2Cl.C(OEt)_3$, by heating $CH_3.CCl_3$ with NaOEt in a sealed tube at 110°. Fragrant liquid. Decomposed by water into alcohol and acetic acid (Geuther, *J.* 1870, 636).

The acetates of the higher alkyls, C_nH_{2n+1}, are analogous in their properties and reactions to ethyl acetate, and are obtained, in like manner, either by heating the corresponding alcohols with acetic and sulphuric acid, or by the action of silver acetate on the corresponding alkyl iodides. The following table shows their boiling points and their S.G. in the liquid state.

	B.P.	S.G.
Propyl Acetates C_3H_7OAc:		
Normal Propyl acetate $Me(CH_2)_2OAc$ or PrOAc	102°	0·913 at 0°
Isopropyl acetate $Me_2CH.OAc$ or PrOAc	90°–93°	
Butyl Acetates C_4H_9OAc:		
Normal Primary: $Me(CH_2)_3OAc$ or CH_2PrOAc	124°	0·9016 "
Isoprimary: $Me_2CHCH_2.OAc$ or CH_2PrOAc	116·5°	0·8596 "
Secondary: Methyl ethyl carbyl acetate MeEtCH.OAc	111°	0·892 "
Tertiary: Trimethyl-carbyl acetate $CMe_3.OAc$	96°	
Amyl Acetates $C_5H_{11}OAc$:		
Normal Primary: $Me(CH_2)_4.OAc$	148·4°	0·8963 "
Isoprimary: $Me_2CH(CH_2)_2OAc$	137°	0·8837 "
Secondary: Diethyl-carbyl acetate $Et_2CH.OAc$	132°	0·9090 "
Methyl-isopropyl-carbyl acetate MePrCHOAc	125°	
Methyl-propyl-carbyl acetate MePrCHOAc	133°	0·9222 "
Tertiary: Dimethyl-ethyl-carbyl acetate $Me_2EtC.OAc$	125°	0·8909 "
Hexyl Acetates $C_6H_{13}OAc$:		
Normal Primary: $Me(CH_2)_5OAc$	169·5°	0·8890 at 17°
Secondary: Methyl-butyl-carbyl acetate $Me(CH_2)_3CHMe.OAc$	155°–157°	0·8778 at 0°
Methyl-tert-butyl-carbyl or Pinacolyl acetate $Me.CHOAc.CMe_3$	140°–143°	
Ethyl-propyl-carbyl acetate EtPrCHOAc	150°	
Heptyl Acetates:		
Normal from *n*-heptane	180°	
Do. from Œnanthol	192°	0·874 at 16°
Methyl-amyl-carbyl acetate $Me(C_5H_{11})CH.OAc$	170°	
Methyl-iso-amyl-carbyl acetate $Me(C_5H_{11})CH.OAc$	167°	0·860 at 23°
Ethyl-iso-butyl-carbyl acetate $Et(C_4H_9)CHOAc$	163°	
Octyl Acetates:		
Normal (from oil of *Heracleum*)	207°	0·872 at 16°
Methyl-hexyl-carbyl acetate $Me(C_6H_{13})CH.OAc$	192°	
Ennyl Acetates:		
From Ennane in petroleum	210°	
Ethyl-hexyl-carbyl acetate $Et(C_6H_{13})CHOAc$	211°	0·878 at 0°
Decyl Acetate:		
Normal $C_{10}H_{21}OAc$. Crystalline. (125°) at 15 mm.		
Dodecyl Acetate:		
Normal $C_{12}H_{25}OAc$. Solid. (151°) at 15 mm.		
Cetyl Acetate:		
$C_{16}H_{33}OAc$. Needles. [18·5°] (200°) at 15 mm.		
Octadecyl Acetate:		
$C_{18}H_{37}OAc$. [31°] (223°) at 15 mm.		
Iso-ceryl Acetate:		
$C_{27}H_{55}OAc$ [57°]		

Allyl Acetate *v.* ALLYL ACETATE.
Phenyl Acetate *v.* PHENOL.
Benzyl Acetate *v.* BENZYL ACETATE.
Methylene Di-acetate *v.* FORMIC ALDEHYDE.
Ethylene Acetates *v.* GLYCOL.
Polyethylenic Acetates *v.* GLYCOL.
Ethylene Aceto-butyrate *v.* GLYCOL.
Ethylene Aceto-chloride *v.* GLYCOL.
Propylene Acetate *v.* PROPYLENE-GLYCOL.
Butylene Acetate *v.* OXY-BUTANES.
Amylene Acetate *v.* OXY-PENTANES.
Glyceryl Acetates *v.* GLYCERIN.

Substitution products of Acetic Acid v. BROMO-ACETIC ACIDS, CHLORO-ACETIC ACIDS, IODO-ACETIC ACIDS, CYANO-ACETIC ACID, SULPHO-CYANO-ACETIC ACIDS, SULPHO-ACETIC ACID.

Other derivatives of Acetic Acid v. ACETYL BROMIDE, BROMO-ACETYL BROMIDE, CHLORO-ACETYL BROMIDE, CYANO-ACETYL BROMIDE, ACETYL CYANIDE, ACETYL CHLORIDE, ACETYL IODIDE, DI-AZO-ACETIC ACID. H. W.

ACETIC BROMIDE *v.* ACETYL BROMIDE.
ACETIC CHLORIDE *v.* ACETYL CHLORIDE.
ACETIC CYANIDE *v.* ACETYL CYANIDE.
ACETIC IODIDE *v.* ACETYL IODIDE.

ACETIC OXIDE or **ANHYDRIDE** $C_4H_6O_3$ or Ac_2O.—*Acetyl oxide, Acetic acid, Anhydrous acetic acid.*—M.w. 102. (137·8°) at 755 mm. (Kopp.); (44·6) at 15 mm., (136·4°) at 760 mm. (Kahlbaum). S.G. $\frac{0}{}$ 1·097, $\frac{152}{}$ 1·799 (K.); $\frac{20}{4}$ 1·0816 (Brühl). V.D. 3·47 (for 3·51). μ_β 1·3953. R_∞ 35·82 (B.). H.F.p. 132,850. H.F.v. 130,820.

Formation. — 1. By the action of phosphorus trichloride or oxychloride on potassium acetate, $3KOAc + POCl_3 = K_3PO_4 + 3AcCl$, and $AcCl + KOAc = KCl + Ac_2O$ (Gerhardt, 1853, *C. R.* 34, 755, 902; *A. Ch.* [3] 37, 285).—2. From potassium acetate and benzoyl chloride, the first product of the reaction being acetobenzoic oxide, which, if the potassium acetate is somewhat in excess, and the mixture is heated to a temperature somewhat above that required for its formation, is resolved into acetic and benzoic oxides: $KOAc + BzCl = KCl + AcOBz$; and $2AcOBz = Ac_2O + Bz_2O$. Similarly from potassium benzoate and acetyl chloride (Gerhardt).—3. By digesting glacial acetic acid and acetyl chloride in molecular proportions (Kanonnikoff a. Saytzeff, *A.* 185, 192).—4. From lead or silver acetate and carbon bisulphide

$$2Pb(OAc)_2 + CS_2 = 2PbS + 2Ac_2O + CO_2$$

(Broughton, *Z.* 1865, 306).—5. From acetal chloride and barium oxide at 100° (Gal).—6. In small quantity by the action of phosphoric anhydride on glacial acetic acid (Gal; Etard, *B.* 9, 444).—7. By the action of lead nitrate on acetyl chloride (Lachowicz, *B.* 17, 1281).

Preparation.—1. Acetyl chloride (1 pt.) is run into sodium acetate (1 pt.) or potassium acetate (1¼ pt.), and the product is distilled. As, however, acetyl chloride is formed by the action of the chlorine compounds of phosphorus on acetates, it is clear that, for the preparation of the anhydride, this chloride need not be quite free from phosphorus oxychloride. It is sufficient, indeed, to add $POCl_3$ (3 pts.) directly to an excess of NaOAc (10 pts.) or KOAc (12 pts.) and distil; or to prepare a mixture of $POCl_3$ and AcCl, by the action of PCl_5 (7 pts.) on glacial acetic acid (2 pts.), and distil this mixture with NaOAc (20 pts.) or KOAc (24 pts.). In all these modes of preparation it is necessary to heat the mixture strongly towards the end of the distillation, because a portion of the acetic oxide unites with the excess of metallic acetate present, forming a compound which requires a high temperature to decompose it. The acetic oxide thus obtained must be subjected to fractional distillation to free it from residual chlorides and acetic acid (Kekulé, *Lehrb.* 1, 570).—2. Hentschel (*B.* 17, 1285) prepares acetic anhydride by passing a stream of carbonyl chloride, $COCl_2$, into fused dry sodic acetate.

Properties.—Colourless, very mobile, strongly refracting liquid, having an odour like that of glacial acetic acid, but stronger.

Reactions.—1. With HCl-gas acetic oxide acts strongly at 100°, forming acetic acid and chloride: $Ac_2O + HCl = AcOH + AcCl$ (Gal, *A. Ch.* [3] 66, 187).—2. With *chlorine* at 100° the products are acetyl chloride and chloracetic acid:

$$(C_2H_3O)_2O + Cl_2 = C_2H_3OCl + C_2H_3ClO_2$$

(Gal). Similarly with Br. With *iodine* no action at 200°, but at higher temperatures HI is given off (Gal).—3. With PCl_5, it yields acetyl chloride: $Ac_2O + PCl_5 = POCl_3 + 2AcCl$. — 4. Heated with solid *aluminium chloride* it forms acetyl chloride and aluminium acetate:

$$3Ac_2O + AlCl_3 = 3AcCl + Al(OAc)_3$$

(Andrianowsky, *J. R.* 11, 116).—5. With pulverised *zinc chloride* at 100° it yields acetic acid, acetic oxide, and a dark brown residue having the composition C_4H_2O (Bauer, *J.* 1861, 438).—6. By heating with *zinc-dust* it yields acetone (Jahn, *M.* 1, 696).—7. Reduced by *sodium amalgam* it forms aldehyde, and afterwards alcohol:

$$(CH_3CO)_2O + 2H_2 = 2CH_3CHO + H_2O;$$
$$2CH_3CHO + 2H_2 = 2CH_3CH_2OH$$

(Linnemann, *A.* 148, 249).—8. Heated in CO_2-gas at 60° with $Cl.SO_2.OH$, it forms an acid, C_2H_6SO, (Gal).—9. With *urea*, at the boiling-point, it forms acetyl carbamide, $NHAcCO.NH_2$. No reaction with *oxamide* (Scheitz; Marsh a. Geuther, *Bl.* [2] 10, 460).—10. With nascent *zinc-ethyl* (2 mol. EtI and 1 mol. Ac_2O added to zinc-sodium) it yields methyl-ethyl ketone:

$$(COMe)_2O + ZnEt_2 = ZnO + 2(Me.CO.Et).$$

With *zinc-methyl* in like manner: acetone, Me.CO.Me (Saytzeff, *Z.* [2] 6, 104).—11. Forms crystalline compounds with $NaHSO_3$ and with NH_3. The latter is formed by passing NH_3 into an ethereal solution of Ac_2O at −20° (Loir, *C. R.* 88, 812).—12. Gives a mirror with ammoniacal $AgNO_3$ (Loir).—13. Decolorises aqueous $KMnO_4$ (Loir).—14. Converted by H_2SO_4 at 130° into sulpho-acetic acid (Franchimont, *C. R.* 92, 1054).

Compounds.—A. With *potassic acetate* $Ac_2O2KOAc$, obtained by dissolving dry potassium acetate in Ac_2O at 100°, crystallises in needles, and is resolved into its constituents by heat (Gerhardt). B. With *aldehydes*.—(1.) With *acetaldehyde* acetic oxide forms the compounds $C_2H_4OAc_2O$ and $C_2H_4O2Ac_2O$. The first is obtained by heating its constituents together in molecular proportion at 180° in a sealed tube, and purified by fractional distillation, washing the portion which distils above 140° with hot water, and drying over $CaCl_2$. It is a liquid which boils at 168°, has an alliaceous odour, and is resolved by heating with KOH into acetic acid and aldehyde—distinction from the isomeric compound, ethylene acetate

$C_2H_4(OAc)_2$, which, when similarly treated, yields glycol, $C_2H_4(OH)_2$ (Geuther, *A.* 106, 249). The second compound, $C_2H_4O.2Ac_2O$, formed by heating paraldehyde with Ac_2O at 160°, is a liquid having a density of 1·07 at 10° (Geuther, *J.* 1864, 329). (2.) With *acrolein.*—The compound $C_3H_4OAc_2O$ is obtained by heating its components in molecular proportion at 100° for six hours, or 1 mol. acroleïn chloride with 2 mols. silver acetate at about 160°. Liquid immiscible with water, having a fishy odour and very sharp taste. S.G. 1·076 at 22°; (180°). $C_3H_4O2Ac_2O$, formed by heating metacroleïn with Ac_2O at 150°, is an oily liquid boiling at 180° (Hübner a. Geuther, *A.* 114, 35; *J.* 1860, 306). (3.) With *benzaldehyde.*—$C_7H_6OAc_2O$ is formed on heating bitter-almond oil with excess of Ac_2O at 150°, and separates on washing the product with water and potash as an oily liquid, which solidifies to a crystalline mass melting at 44°–45° (Hübner, *Z.* [2] 3, 277). These compounds may be looked upon as derived from *ortho-aldehydes*, $XCH(OH)_2$. Similar compounds will be described in articles on the several aldehydes. C. With other oxides.—Vapour of SO_3 is absorbed by cooled Ac_2O, forming a gummy mass soluble in water. *Boric oxide* dissolves slowly in Ac_2O, forming a vitreous hygroscopic mass. *Insoluble tartaric oxide* or *anhydride*, $C_4H_4O_5$, dissolves at 100° in acetic oxide, forming a syrup. The same syrupy product is formed, together with $PbCl_2$, by the action of AcCl on lead tartrate.

Aceto-arsenious Oxide $C_4H_6O_3As_2O_3$ or $Ac.O.OAs$ is formed by dissolving As_2O_3 in acetic oxide at boiling heat, as a syrupy liquid, which on cooling forms a vitreous hygroscopic mass.

Aceto-hypochlorous Oxide AcOCl and *Aceto-hypoiodous Oxide* AcOI have been described as unstable compounds by Schützenberger (*C. R.* 52, 359; 54, 1026; *J.* 1862, 240), but their existence has been called in question by Aronheim (*B.* 12, 26).

Aceto-silicic Oxide $Si(OAc)_4$ [110°] (148°) at 6mm. From Ac_2O and SiO_2 (Friedel a. Ladenburg, *A.* 145, 174). Decomposed by water, heat, alcohol, or NH_3, into silica and $HOAcAc_2O$, EtOAc, and NH_2Ac, respectively. A compound, $Si(OEt)_3(OAc)$ (c. 195°), is formed from $Si(OEt)_4$ and Ac_2O.

Aceto-benzoic Oxide $C_9H_8O_3$ i.e. AcOBz, from acetyl chloride and sodium benzoate, is a heavy oil. Begins to boil at 150°, and is resolved at the same time into Ac_2O and Bz_2O. By boiling with water, and more quickly with alkalis, it is converted into acetic and benzoic acids (Gerh. 3, 209). HCl converts it at low temperatures into AcCl and HOBz; at 150° BzCl and HOAc are also formed. Chlorine forms AcCl and o-chloro-benzoic acid (Greene, *C. N.* 50, 61).

Aceto-cinnamic Oxide $Ac.O.C_9H_7O$. Obtained like the preceding, which it resembles. Oil, heavier than water, very unstable (Gerhardt, *ib.* 387).

Aceto-cuminic Oxide $Ac.O.C_{10}H_{11}O$. Like the preceding (Gerhardt, *ib.* 509).

Aceto-salicylic Oxide $Ac.O.C_7H_5O_2$. Solid; dissolves in aqueous sodium carbonate, with formation of sodium acetate and salicylate (Gerhardt, *ib.* 319).

Acetic Peroxide $C_4H_6O_4$ or Ac_2O_2.—Prepared by adding BaO_2 to a solution of acetic anhydride in ether. The mixture is effected gradually, being attended with evolution of heat. The ether is distilled off at a low temperature, and the fluid which remains is washed with water. It is a viscid liquid with pungent taste. It decolorises indigo, oxidises manganous hydrate to peroxide, and potassic ferro- to ferricyanide. It acts generally as an oxidising agent. It does not reduce CrO_3 or $KMnO_4$. Baryta-water is converted by it into barium peroxide and acetate. It explodes when heated (Brodie, *Pr.* 9, 363). H. W.

ACET-IMIDAMIDE *v.* ACETAMIDINE.

ACET-IMIDO-ETHYL-ETHER

$$CH_3.C\begin{matrix}\diagup\!\!\!\diagup NH\\ \diagdown OEt\end{matrix}$$

(97°). Liquid. The hydrochloride is obtained by passing dry HCl-gas into a mixture of acetonitrile and ethyl alcohol (equal mols.) diluted with $\frac{1}{3}$ their volume of ether, cooled to 0° C. B′HCl, long trimetric plates, decomposes at about 100° into ethyl chloride and acetamide (Pinner, *B.* 16, 1654).

ACETIMIDO-NAPHTHYL-AMIDE *v.* NAPHTHYL-ACETAMIDINE.

ACETIMIDO-TOLYL-AMIDE *v.* TOLYL-ACETAMIDINE.

ACETO-ACETIC ACID $CH_3.CO.CH_2.CO_2H$ or $CH_3.C(OH):CH.CO_2H$.

Occurrence.—In urine of diabetic patients (Geuther a. Rupstein, *Fr.* 14, 419; Deichmüller, *A.* 209, 30; Tollens, *A.* 209, 36; Jaksch, *H.* 7, 487).

Preparation.—The ethyl ether (4·5 g.) is mixed with water (80 g.) containing KOH (2·1 g.), and after 24 hours the liquid is acidified and shaken with ether (Ceresole, *B.* 15, 1327, 1872).

Properties.—A thick acid liquid, miscible with water. At 100° it splits up into CO_2 and acetone. Nitrous acid gas forms CO_2 and iso-nitroso-acetone.

Salts.—BaA'_2aq. Amorphous. V.e. sol. water. Violet colour with $FeCl_3$.—$CuA'_2$2aq. Amorphous.

Ethyl Aceto-acetate or *Aceto-acetic Ether* $CH_3.CO.CH_2.CO_2Et$ or $CH_3.C(OH):CH.CO_2Et$. *Di-acetic ether* (Geuther, *J.* 1863, 323), *ethyl-di-acetic acid* (Geuther, *J.* 1865, 302), *acetone-carboxylic acid* (Frankland a. Duppa, *A.* 138, 211) (180°) (R. Schiff, *B.* 19, 561); (180·8° cor.) (Geuther); (180·6°–181·2°) at 754 mm. (Brühl); (152·5°–153°) at 330 mm. (Perkin). S.G. $\frac{20}{4}$ 1·0256 (B.); $\frac{0}{4}$ 1·046 (S.); $\frac{15}{15}$ 1·0317 (P.); $\frac{25}{25}$ 1·0235 (P.). μ_β 1·4253. R_∞ 51·62 (B.). S.V. 153·34 (S.). M.M. 6·501 at 16·25 (P.).

Formation.—The formation of aceto-acetic ether by the saponification of cyano-acetone by alcoholic HCl (Matthews a. Hodgkinson, *B.* 15, 2679) is denied by James (*A.* 231, 245).

Preparation.—Ethyl acetate (1 kilo.), that has been carefully dried, is treated with sodium (100 g.) in small pieces. As soon as the first reaction abates it is heated with inverted condenser over a water bath for $2\frac{1}{2}$ hours until the sodium is dissolved. Dilute (50 p. c.) acetic acid (550 g.) is then added, and when the liquid is cool, it is mixed with water (500 c.c.). The light oily layer is washed with a little water and fractioned. The yield (175 g.) is small, but much ethyl acetate (400 g.) is recovered (Conrad, *A.* 186, 214). Aceto-acetic ether may be still further purified

by shaking with conc. aqueous $NaHSO_3$, with which it combines. Impurities may then be extracted by ether, and the compound of aceto-acetic ether with $NaHSO_3$ afterwards decomposed by K_2CO_3 (Elion, *R.* 3, 246).

The formation of aceto-acetic ether may be expressed by the equation:

$$2CH_3.CO_2Et + Na_2 =$$
$$CH_3.CO.CHNa.CO_2Et + NaOEt + H_2,$$

the sodio-aceto-acetic ether being afterwards decomposed by the added acetic acid:

$$CH_3.CO.CHNa.CO_2Et + HOAc =$$
$$CH_3.CO.CH_2.CO_2Et + NaOAc.$$

See also p. 21.

Properties.—A liquid with an agreeable sweet odour. Slightly soluble in water, the liquid giving a violet colour with $FeCl_3$. Unlike its ethyl and acetyl derivatives, it forms a crystalline compound with $NaHSO_3$ (indicating presence of the ketonic carbonyl group, CO).

Salts.—Aceto-acetic ether behaves as a monobasic acid. This may either be ascribed to the situation of the group CH_2 between two CO groups, or else by having recourse to the formula $CH_3.C(OH):CH.CO_2Et$, which represents a compound that might be expected, as a tertiary alcohol, to possess a phenolic character. Like phenol, it gives a violet colour with $FeCl_3$.

Sodio-aceto-acetic Ether $CH_3.CO.CHNa.CO_2Et$ or $CH_3.C(ONa):CH.CO_2Et$. Needles. Produced by the action of sodium or sodic ethylate upon aceto-acetic ether in the cold.

Preparation.—Sodium (10 g.) is dissolved in absolute alcohol (100 g.); when cold, dry ether (90 g.), followed by aceto-acetic ether (56·5 g.) diluted with ether (60 c.c.), is added. If the liquid is well stirred with a little water (2 c.c.) solid sodium acetacetic ether separates (Harrow, *C. J.* 33, 426). The pp. is a hydrate, which becomes dry in an exsiccator (Elion, *R.* 3, 240).

Reactions.—(*a*) With iodine in ethereal solution it gives di-aceto-succinic ether (*q. v.*).—(*b*) Heated alone or with NaOEt it gives acetone, aceto-acetic ether, NaOAc, and sodic dehydracetate.—(*c*) With *alkyl iodides* it forms alkyl-aceto-acetic ethers (*q. v.*):

$$CH_3.CO.CHNa.CO_2Et + R'I =$$
$$NaI + CH_3.CO\ CHR'.CO_2Et.$$

Other iodo- bromo- and chloro- compounds act similarly.—(*d*) But with tri-PHENYL-METHYL BROMIDE Ph_3CBr it forms $CH_3CO.C(CPh_3)_2.CO_2Et$ (Allen a. Kölliker, *A.* 227, 110).—(*e*) Chloroform, in presence of NaOEt forms OXY-UVITIC ETHER: $C_6H_2Me(OH)(CO_2H)_2$ [1 : 3 : 4 : 6], the first stage probably being:

$$2CH_3.CO.CHNa.CO_2Et + NaOEt + CHCl_3 =$$
$$CO_2Et.CHAc.CH:C(CO_2Et).CO.CH_3 + 3NaCl + HOEt$$

(Oppenheim a. Pfaff, *B.* 7, 929; 8, 884; 9, 321; Conrad a. Guthzeit, *A.* 222, 249).

Other Salts.—$Al(C_6H_9O_3)_3$. Needles [76°]. Insol. water, v. e. sol. ether, benzene or CS_2. May be sublimed.—$Co(C_6H_9O_3)_2$. Red pp. Sol. hot benzene or ether.—$Cu(C_6H_9O_3)_2$ [182°]. Green needles (from alcohol). Insol. water, v. sol. benzene, ether or CS_2. Got by adding $Cu(OAc)_2$ to a solution of aceto-acetic ether in alcohol, the calculated quantity of ammonia being also added (Conrad a. Guthzeit, *B.* 16, 19).—$Mg(C_6H_9O_3)_2$ [240°]. From aceto-acetic ether and 'magnesia-mixture.' Plates (from ether-benzene).—$Hg(C_6H_9O_3)_2$ Amorphous. Formed by shaking aceto-acetic ether with HgO.—$Ni(C_6H_9O_3)_2$.

Reactions.—1. Boiled for a long time, or passed through a red-hot tube, it forms dehydracetic acid, $C_8H_8O_4$, and alcohol.

2. Boiled with *alkalis* it gives CO_2, acetone, acetic acid and alcohol, according to the reactions:

$$CH_3.CO.CH_2.CO_2Et + 2KOH =$$
$$CH_3.CO.CH_3 + K_2CO_3 + HOEt;$$
$$CH_3.CO.CH_2.CO_2Et + 2KOH =$$
$$2CH_3.CO.OK + HOEt.$$

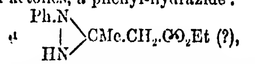
3. Decomposed by water at 150°, or by strong acids, into CO_2, acetone and alcohol.

4. Action of *sodium alcoholates.*—(*a*) Heated with dry NaOEt, or with alcoholic NaOEt, ethyl acetate is got in small quantity (12 p.c. of the theoretical) (Wislicenus, *A.* 186, 193; Isbert, *A.* 234, 160).—(*b*) 50 g. heated with NaOEt (from 8·9 g. Na) and MeOH (75 g.) at 130° gives methyl acetate (7 g.) and ethyl acetate (1 g.). Similar results are obtained by using PrOH instead of MeOH (Isbert).—(*c*) At 130° with NaOPr and excess of MeOH gives methyl acetate and a little propyl acetate.—(*d*) Heated with alcohol at 180° it is not affected, but if a very little NaOEt be present it is completely decomposed, yielding EtOAc. Similar results are got by using PrOH and NaOPr. *Resacetic Acid* $C_{14}H_{22}O_5$ is found in all these cases as a resinous body, not volatile with steam. It forms brown amorphous salts, NaA', KA', and NH_4A', sol. water (Isbert, *A.* 234, 167).

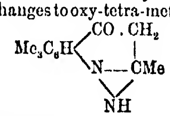
5. *Sodium-amalgam* forms β-oxy-butyric acid:

$$CH_3.CO.CH_2.CO_2Et + H_2 =$$
$$CH_3.CH(OH).CH_2.CO_2Et.$$

6. *Phenyl-hydrazine* in the cold forms, as with all ketones, a phenyl-hydrazide:



but at 100° this loses EtOH and becomes *methyl-oxy-*QUINIZINE (*q. v.*) (Knorr, *B.* 17, 2032). Pseudo-cumyl-hydrazine produces the homologous hydrazide $CH_3.C(N_2HC_6H_2Me_3).CH_2.CO_2Et$ [78°]. Long yellow needles (from alcohol), or thick prisms (from ether). V. sol. hot alcohol or ether, sl. sol. cold alcohol or benzoline. Very unstable, and at 130°–140° changes to oxy-tetra-methyl-quinizine:



(Haller, *B.* 18, 706).

7. *Hydroxylamine* forms, as with other ketones, the oxim: $CH_3.C(NOH).CH_2.CO_2Et$, β-Oximido-butyric acid, $CH_3.C(NOH).CH_2.CO_2H$; colourless crystals, [140°], sl. sol. water, alcohol or ether (Westenberger, *B.* 16, 2996).

8. Fuming *nitric acid* yields oxalic acid and OXIMIDO-ACETO-ACETIC ETHER (*q. v.*) (Pröpper, *A.* 222, 48).

9. *Sulphuryl Chloride* forms mono- or di-chloro-aceto-acetic ether, according to the proportions used (Allihn, *B.* 11, 567):

$$CH_3.CO.CH_2.CO_2Et + SO_2Cl_2 =$$
$$CH_3.CO.CHCl.CO_2Et + SO_2 + HCl;$$
$$CH_3.CO.CH_2.CO_2Et + 2SO_2Cl_2 =$$
$$CH_3.CO.CCl_2.CO_2Et + 2SO_2 + 2HCl.$$

10. *Bromine* gives *mono-*, *di-*, *tri-*, and *per* BROMO-ACETO-ACETIC ETHERS (Wedel, *A.* 219, 071

11. *Chlorine* forms only DI-CHLORO-ACETO-ACETIC ETHER (*q. v.*).

12. *Phosphorus pentachloride* forms the chlorides of two CHLORO-CROTONIC ACIDS (*q. v.*).

13. Dry *prussic acid* heated with aceto-acetic ether for 8 days at 100° forms a cyanhydrin, $CH_3.C(OH)(CN).CH_2.CO_2Et$, which is converted by boiling dilute HCl into oxy-pyrotartaric acid (G. H. Morris, *C. J.* 37, 7).

14. *Cyanogen chloride* passed into sodio-aceto-acetic ether forms CYANO-ACETO-ACETIC ETHER (*q. v.*) $CH_3.CO.CH(CN).CO_2Et$ (Haller a. Held, *C. R.* 95, 235).

15. *Ammonia*, whether dry (Precht, *B.* 11, 1193), aqueous or alcoholic (Duisberg, *A.* 212, 171), produces the imide of aceto-acetic ether.

Aceto-acetic ether imide $C_6H_{11}NO_2$ [34°]. (213° uncor.) at 760 mm., (154°) at 154 mm. S.G. $\frac{20}{}$ 1·014. S. (conc. NH_3Aq) 1·25. Dry NH_3 is greedily absorbed by aceto-acetic ether, the compound $CH_3.C(OH)(NH_2).CH_2.CO_2Et$ being doubtless at first formed. The liquid soon separates into two layers, water and the imide of aceto-acetic ether. The latter is purified by distillation (Collie, *A.* 226, 297). *Properties.*—Colourless monoclinic prisms. V. sl. sol. water, v. sol. alcohol, ether, benzene, CS_2 and $CHCl_3$. Moisture greatly lowers its melting-point. It is $CH_3.C(NH).CH_2.CO_2Et$ or $CH_3.C(NH_2):CH.CO_2Et$. *Reactions.*—(*a*) Aqueous HCl splits it up into NH_3 and aceto-acetic ether (Duisberg).—(*b*) Cold dilute NaOH has no action, but on warming it gives NH_3, HOEt, acetone and CO_2.—(*c*) $Pb(OAc)_2$, $HgCl_2$, $ZnSO_4$, or $FeCl_3$ also splits it into aceto-acetic ether and NH_3, the latter throwing down the metallic hydrate. $AgNO_3$ does not give any pp.—(*d*) Glacial acetic acid also regenerates aceto-acetic ether on boiling.—(*e*) Sodium amalgam gives β-oxy-butyric acid.—(*f*) Nitrous fumes passed into alcoholic solution forms nitroso-aceto-acetic ether. A by-product $C_9H_{17}N_5O_5$, forms plates [170°].—(*g*) Ac_2O at 160° forms an acetyl derivative, $C_6H_{10}AcNO_2$ [63°] (232°), which combines with bromine, forming $C_6H_{10}AcBr_2NO_2$ [140°].—(*h*) Paraldehyde gives di-hydro-tri-methyl-pyridine di-carboxylic acid, which is also formed from aceto-acetic ether, NH_3, and aldehyde.—(*i*) EtI at 100° forms ethyl-aceto-acetic ether and a base (c. 290°), possibly ethoxy-di-methyl-pyridine. *Condensation-products*: $C_{10}H_{13}NO_3$ [160°]. Present in the brown resin got when $C_6H_{11}NO_2$ is distilled under atmospheric pressure. Insoluble in alcohol and ether. Boiled with KOHAq it forms oxy-di-methyl-pyridine carboxylic acid.

16. *Aceto-acetic ether methyl-imide*,
$CH_3.C(NMe):CH_2.CO_2Et$ or
$CH_3.C(NHMe):CH.CO_2Et$,
(133°) at 50 mm., (215°) at 760 mm., is formed in like manner from aceto-acetic ether and *methylamine* (Kuchert, *B.* 18, 618). With paraldehyde and H_2SO_4 it gives a condensation-product, $C_{13}H_{22}O_4N$, which forms trimetric crystals with blue fluorescence [86°].

17. *Diethylamine* forms *β-di-ethyl-amido-crotonic ether*, $CH_3.C(NEt_2):CH.CO_2Et$, a liquid (160°–163°) at 20 mm.

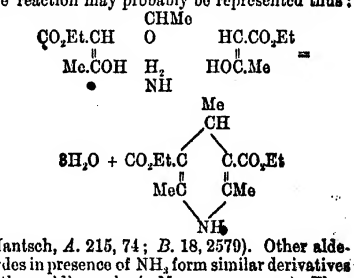
18. Heated with *aniline* (1 mol.) at 120° it yields a crystalline body, $C_{10}H_{11}NO_2$, which melts at 81° and is probably the anilide of acet-acetic acid $CH_3.C(NPh).CH_2.CO_2H$. By dissolving this substance in cold H_2SO_4, H_2O is eliminated with formation of (B. 1)-oxy-(Py. 3)-methyl-QUINOLINE (Knorr, *B.* 16, 2593).

19. *o-Phenylene-diamine* forms:
$$C_6H_4(N:CMe.CH_2.CO_2Et)_2.$$

20. *o-Tolylene-diamine* gives:
$$CH_3.C_6H_3\left\langle{NH \atop NH}\right\rangle CMe.CH_2.CO_2Et.$$
(Ladenburg, *B.* 12, 951; Witt, *B.* 19, 2977).

21. With *aldehydes* (Claisen, *B.* 12, 345):
$$CH_3CO.CH_2.CO_2Et + RCOH = H_2O + CH_3.CO.C(CH.R).CO_2Et.$$
The bodies are mixed in molecular proportions, and HCl is passed in at 0°. Or the bodies may be heated with Ac_2O. Examples (Matthews, *C. J.* 43, 200):—(*a*) *Isobutyric aldehyde* gives $C_{10}H_{16}O_3$ (219°–222°). Oil. Smells like peppermint. Combines with bromine. (*b*) *Valeric aldehyde* gives $C_{11}H_{18}O_3$ (237°–241°). S.G. $\frac{15}{15}$ ·9612. Oil. Smells of strawberries. (*c*) *Chloral* gives $C_8H_9Cl_3O_3$ (151°–158°) at 25 mm. S.G. $\frac{15}{15}$ 1·3420. From chloral, acet-acetic ether, and Ac_2O at 150°. (*d*) *Furfural* gives $C_{11}H_{12}O_4$ [62°], (188°–189°) at 30 mm. From furfural, acet-acetic ether, and Ac_2O. Easily soluble in chloroform, acetic acid, alcohol, and benzene. Large doubly-refracting crystals (from light petroleum and ether).

22. Aceto-acetic ether (2 mols.) condenses with *aldehyde-ammonia*, forming DI-HYDRO-TRI-METHYL-PYRIDINE-DI-CARBOXYLIC ETHER (*q. v.*):
$$2CH_3.CO.CH_2.CO_2Et + CH_3.CH(OH)NH_2 = 3H_2O + C_5H_2NMe_3(CO_2Et)_2.$$
Since the product contains three methyls and two CO_2Et groups, we may assume these to be identical with the same groups in the reacting bodies. And inasmuch as the product is not acted upon by nitrous acid gas and forms an ammonium iodide with MeI, it would seem to be a tertiary base. Nevertheless, inasmuch as methylamine and aldehyde give a similar body, the reaction may probably be represented thus:



(Hantsch, *A.* 215, 74; *B.* 18, 2579). Other aldehydes in presence of NH_3 form similar derivatives of the pyridine series (*v.* METHYL-PYRIDINE). Thus *cinnamic aldehyde* and ammonia forms di-methyl-styryl-di-hydro-pyridine di-carboxylic ether, $H_2C_5NMe_2(CH:CHPh)(CO_2Et)_2$, [148°] (Epstein, *A.* 231, 3).

23. With *formamide* and $ZnCl_2$ aceto-acetic ether gives di-methyl-pyridine carboxylic ether (Canzeroni a. Spica, *G.* 14, 449).

24. With *acetamide* and $AlCl_3$ it forms $CH_3.C(NAc).CH_2.CO_2Et$ [65°]. Needles. Converted by KOH into the amide of aceto-acetic ether.

25. Mixing with *acetamidine hydrochloride* and dilute NaOH, and, after standing for some days, evaporating to dryness and extracting with alcohol, yields a di-methyl-oxy-pyrimidine,

$C_6H_8N_2O$ [190°]. Needles. V. sol. water or alcohol, sl. sol. ether or benzene. It is probably

$$CH_3.C\genfrac{}{}{0pt}{}{\nearrow N\,.\,CMe \searrow}{\searrow N{:}C(OH) \nearrow}CH.$$

Propionamidine forms a homologue, methyl-ethyl-oxy-pyrimidine [130°]. Its hydrochloride forms thick prisms, $C_7H_{10}N_2OHCl$ [c. 243°]. V. e. sol. water, v. sol. alcohol—$(C_7H_{10}N_2OHCl)_2PtCl_4$ [236°]. Prisms. (Pinner, *B.* 17, 2520; 18, 2847).

26. With *urea* in alcoholic solution it forms *β*-uramido-crotonic ether (Behrend, *A.* 229, 5):

$$MeC(OH){:}CH.CO_2Et + NH_2.CO.NH_2 = NH_2.CO.NH.CMe{:}CH.CO_2Et + H_2O.$$

The free β-URAMIDO-CROTONIC ACID, when liberated from its salts, changes at once into its anhydride, methyl-uracil:

$$\underbrace{NH.CO.NH.CMe{:}CH.CO}$$

27. *Thio-urea* (40 g.), heated with aceto-acetic ether (40 g.) slowly to 150°, gives a compound $C_5H_6N_2OS$ (5 g.), which may be *thio-methyl-uracil*. It may be crystallised from water. It dissolves in alkalis and is reppd. by acids. Its melting-point lies above 300°. Its aqueous solution gives with $AgNO_3$ an amorphous pp. of $C_5H_4Ag_2N_2SO$ (Nencki a. Sieber, *J. pr.* [2] 25, 72). If a little HCl be added to an alcoholic solution of thio-urea and aceto-acetic ether, unstable needles are formed. These are converted by alcoholic potash into potassium thio-methyl-uracil, $C_5H_5KN_2SO$ (List, *B.* 19, 219).

28. Aceto-acetic ether (20 g.), *phenyl-urea* (10 g.), and ether (6 g.) at 150° react thus:

$$C_6H_{10}O_3 + C_7H_8N_2O = C_{13}H_{16}N_2O_3 + H_2O.$$

The product is an oil which is decomposed by alcoholic potash with formation of ammonia and aniline, and by boiling conc. HCl with formation of CO_2, alcohol, acetone, and phenyl-carbamic ether, $PhNH.CO_2Et$. The reactions indicate that the body $C_{13}H_{16}N_2O_3$ has the constitution $NPhH.CO.N{:}CMe.CH_2.CO_2Et$, or perhaps

$$CO\genfrac{}{}{0pt}{}{\nearrow NH \searrow}{\searrow NPh \nearrow}CMe.CH_2.CO_2Et$$

(Behrend, *A.* 233, 1).

29. Combines directly with *di-phenyl-urea*, in presence of a little ether at 150°, forming an oil, $C_{19}H_{22}N_2O_4$. This body is converted by alcoholic KOH into aniline and K_2CO_3, and by acids into phenyl-carbamic ether and aniline. The body must be

$$PhNH.CO.NPh.C(OH)Me.CH_2.CO_2Et.$$

Similar addition products are probably first formed in the case of other ureas, but H_2O splits off:

$$PhNH.CO.NH.C(OH)Me.CH_2.CO_2Et = H_2O + PhNH.CO.N{:}CMe.CH_2.CO_2Et.$$

30. *p-Di-azo-toluene Chloride*, acting on an alcoholic solution of aceto-acetic ether, forms yellow needles of *p*-toluene-azo-aceto-acetic ether [188°] $C_6H_4Me.N_2.CH(CO.CH_3).CO_2Et$ (Richter a. Münzer, *B.* 17, 1929; *v.* AZO compounds).

31. *Hydrazo-benzene* at 100°–150° forms HOEt and a crystalline base, $C_{16}H_{14}N_2O$ (A. Müller, *B.* 19, 1771).

32. Copper aceto-acetic ether is converted by $COCl_2$ into an anhydride of di-acetyl-acetone di-carboxylic ether, $CO(CHAc.CO_2Et)_2$. The anhydride may be:

$$\begin{array}{c} CH_3.C - O - C.CH_3 \\ \| \qquad\qquad \| \\ CO_2Et.C - CO - C.CO_2Et. \end{array}$$

[80°]. Sol. glacial HOAc, H_2SO_4, conc. HCl, benzene, alcohol, or ether. NH_3 converts this body into oxy-di-methyl-pyridine-di-carboxylic ether

$$\begin{array}{c} CH_3.C - NH - C.CH_3 \\ \| \qquad\qquad \| \\ CO_2Et.C - CO - C.CO_2Et \end{array}$$

(Conrad a. Guthzeit, *B.* 19, 22).

33. Aceto-acetic ether, heated with CS_2 and PbO at 100°, forms 'thio-carbonyl-aceto-acetic ether' $CH_3.CO.C(CS).CO_2Et$ [156°–162°]. Yellow needles (from alcohol) (Norton a. Oppenheim, *B.* 10, 703).

34. S_2Cl_2 converts sodium aceto-acetic ether suspended in benzene into sulphido-aceto-acetic ether $S(CHAc.CO_2Et)_2$ [81°] (Buchka, *B.* 18, 2092).

35. With *succinic acid* it reacts thus:

$$C_6H_{10}O_3 + C_4H_6O_4 = C_{10}H_{12}O_5 + 2H_2O.$$

The product is a crystalline acid [76°], which is the acid ether of a dibasic acid $C_8H_8O_5$ [200°] (Fittig, *B.* 18, 2526).

Condensation products from aceto-acetic ether.—1. By *heat*: Passed through a red-hot tube it forms DEHYDRO-ACETIC ACID (*q. v.*) and other products (Perkins, jun. *C. J.* 47, 240).—2. By *hydrochloric acid*: Dry HCl at 8° forms, in four weeks, acetic ether and 'carb-aceto-acetic ether' $C_8H_{10}O_3$ (290°–295° uncor.). S.G. $\frac{27}{}$ 1·136. This liquid is slightly decomposed on distillation. It gives no colour with aqueous Fe_2Cl_6 (Duisberg, *A.* 213, 179). Carb-aceto-acetic ether is also formed when aceto-acetic ether is heated with acetyl chloride at 120° (Wedel, *A.* 219, 110).—3. By *sulphuric acid*:

$$C_6H_7(OH)(CO_2H).CO.O.C_6H_7(CO_2H)(CO_2Et)$$

[62°]. Got by leaving a mixture of aceto-acetic ether (1 pt.) and cold conc. H_2SO_4 ($2\frac{1}{2}$ pts.) for fourteen days and then pouring into water (Hantzsch, *A.* 222, 4). Needles resembling asbestos. Sl. sol. cold water, m. sol. hot water and ether, v. sol. alcohol, v. e. sol. chloroform. Decomposed by heat. It is acid to litmus and, when hot, has a spicy odour. Its formation may be represented thus:

$$4C_6H_{10}O_3 = C_{18}H_{22}O_9 + 3C_2H_5OH.$$

Reactions.—(*a*) Boiling alkalis form carbonate and acetate, acetone, and mesityl oxide. (*b*) On neutralising with alcoholic potash it decomposes thus:

$$C_6H_7(OH)(CO_2H).CO.O.C_6H_7(CO_2H)CO_2Et + KOH = C_6H_7(CO_2K)\genfrac{}{}{0pt}{}{\nearrow O \searrow}{\searrow CO \nearrow} + C_6H_7(CO_2Et)\genfrac{}{}{0pt}{}{\nearrow O \searrow}{\searrow CO \nearrow} + 2H_2O,$$

the potassium salt of mesitene-lactone carboxylic acid being ppd. while its ether remains in solution.

Mesitene-lactone Carboxylic Acid

$$\underbrace{CH_3.C{:}C(CO_2H).CMe{:}CH.CO.O}$$

[155°] (iso-dehydracetic acid). Fluffy crystals (from water). Sl. sol. cold water, v. sol. hot water. Monoclinic prisms (from alcohol). May be sublimed.

Reactions.—Distilled with lime it gives mesityl oxide.

Salts.—$KA'\frac{1}{2}aq.$ — NaA'.— NH_4A' — BaA'_2.— MgA'_2.— $CuA'_2 2aq.$—$Ag_4H_2A'_3$.—$Ag_2HA'_?$. Strong

bases convert iso-dehydracetic acid into oxy-mesitene dicarboxylic acid,

$CH_3.C(OH):C:C(CO_2H).CMe:CH.CO_2H$,

which forms a stable copper salt $Cu_3H_2A''_4$, but its alkaline salts readily split off CO_2:

$C_6H_7(OH)(CO_2Na)_2 + NaOH =$
$C_6H_8(OH)(CO_2Na) + Na_2CO_3$,

forming oxy-mesitene carboxylates. These readily undergo a similar decomposition:

$C_6H_8(OH)(CO_2Na) + NaOH = Na_2CO_3 + C_6H_9OH$,

probably forming 'mesitenyl' alcohol, which at once changes to mesityl oxide. Baryta is the best alkali to use in these decompositions.

Mesitene Lactone
$CH_3.C:CH.CMe:CH.CO.O$

[51·5°] (245° cor.). From iso-dehydracetic acid by distillation, or by heating with H_2SO_4 at 170°. Glittering tables. Very soluble in alcohol, ether, or water, sparingly so in CS_2. Tastes bitter and spicy. Neutral to litmus. Separated by K_2CO_3 from aqueous solution. Gives with Br in CS_2 a bromo-derivative, $C_6H_7BrCO_2$ [105°]. Converted even by water into oxy-mesitene carboxylic acid. Hence it is a δ-lactone.

Oxy-mesitene Carboxylic Acid
$C_6H_8(OH)(CO_2H)$ *i.e.*
$CH_3.C(OH):CH.CMe:CH.CO_2H$.

From its lactone (mesitene-lactone) by boiling with water or, better, with baryta. A thick liquid, soluble in water. Its salts are amorphous, *e.g.* BaA'_2, CaA'_2. These salts on boiling form carbonate and mesityl oxide.

Mesitene-lactone Carboxylate of Ethyl
$C_6H_7(CO_2Et)CO_2$ *i.e.*
$CH_3.C:C(CO_2Et).CMe:CH.CO.O$.

Formed, together with its potassium salt, by the action of alcoholic KOH on the product of condensation of aceto-acetic ether, as described above. Also from its potassium salt by EtI. Also got when aceto-acetic ether, saturated with HCl, is left at 0° for a month (Polonowska, *B.* 19, 2402). Oil. *Reactions.*—(*a*) Br in CS_2 forms $C_6H_6Br(CO_2Et)CO_2$ [87°]. Needles (from alcohol). —(*b*) NH_3 passed into an alcoholic solution forms satiny plates of $C_6H_7(CO_2Et)(CO.NH_2)(ONH_4)$ melting at [104°], giving off $2NH_3 + H_2O$, and changing to the lactone. Warm water or cold alcohol also change it to the lactone. Cold HClAq liberates $C_6H_7(CO_2Et)(CO_2H)(OH)$, which may be extracted by ether. Small plates [76°]. Boiled with water, two-thirds are changed to lactone, and when the lactone is boiled with water, one-third becomes oxy-acid. It forms salts of the form $C_6H_7(OH)(CO_2Et)(CO_2H)$, viz. CuA'_2aq, PbA'_2aq. When the acid is boiled with alkali there is formed dehydracetic acid and its decomposition products, mesityl oxide, acetone, and CO_2, and the following decomposition also occurs:

$CH_3.C:C(CO_2Et).CMe:CH.CO.O + 3H_2O =$
$CH_3.CO_2H + HOEt + CH_2(CO_2H).CMe:CH.CO_2H$,

resulting in homomesaconic acid.

Homomesaconic Acid
$CH_2(CO_2H).CMe:CH.CO_2H$

[147°]. Small prisms (from water). V. sol. cold water, and alcohol, sl. sol. ether. Not volatile with steam, but sublimes about 120°.

Salts.—$BaA''4\frac{1}{2}aq$.—$CaA''aq$.—$CuA''2aq$.—Ag_2A''.—KHA''.—NH_4HA''.

Ethyl ether Et_2A''. (240°–242°).

Theory of the Condensation.—As acetone gives mesityl oxide $C_6H_{10}O$ or $CH_3.CO.CH:C(CH_3)_2$, so aceto-acetic ether, if it is $CH_3.CO.CH_2CO_2Et$, should give the dicarboxylic ether of mesityl oxide, $C_6H_8O(CO_2Et)_2$, or the acid, $C_6H_8O(CO_2H)_2$. Instead of this, it gives an isomeride of the latter, $C_6H_7(OH)(CO_2H)_2$, so that the group CO.CH must have changed to C(OH):C. Assuming that this group pre-exists in aceto-acetic ether, the condensation would be as follows:

$CH_3.C(OH):C(CO_2Et)H + HO.CMe:CH.CO_2Et =$
$CH_3.C(OH):C(CO_2Et).CMe:CH.CO_2Et + H_2O =$
$CH_3.C:C(CO_2Et).CMe:CH.CO.O + HOEt + H_2O$.

Acetyl-aceto-acetic Ether
$CH_3.CO.CHAc.CO_2Et$ or $CH_3.C(OAc):CH.CO_2Et$, *di-aceto-acetic ether.* (200°–205°). S.G. $\frac{15}{15}$ 1·064 (James); $\frac{15}{}$ 1·101 (Elion). From aceto-acetic ether (65 g.), ether (50 g.) and sodium (9 g.), by adding a solution of AcCl (30 g.) in ether (50 g.) in the cold (J. W. James, *A.* 226, 210; *C. J.* 47, 1).

Properties.—Pleasant smelling liquid, slightly decomposed on distillation. Miscible with alcohol, ether, and benzene, hardly soluble in water, but slowly decomposed by it into acetic acid and aceto-acetic ether. Fe_2Cl_6 gives a raspberry-red colour, removed by SO_2.

Salts.—Acetyl-aceto-acetic acid is a strong acid, and can expel acetic acid from its salts. —CuA'_22aq: insoluble in water; [148°].—NaA' (Elion, *R.* 3, 255).—NiA'_22aq.

Reactions.—1. NaOEt decomposes it into EtOAc and sodium aceto-acetic ether.

Benzoyl-aceto-acetic Ether
$CH_3.CO.CBzH.CO_2Et$

From sodium aceto-acetic ether and benzoyl chloride alone (Bonné, *A.* 187, 1), or dissolved in ether (James, *A.* 226, 220; *C. J.* 47, 10).

Properties.—A fairly strong acid, capable of displacing acetic acid.

Salt.—CuA'_2 (from benzene) [180°–190°]. Formed by shaking the ether with aqueous cupric acetate. Sl. sol. alcohol or benzene, m. sol. ether.

o-**Nitro-benzoyl-aceto-acetic Ether.**—Prepared as above, using nitro-benzoyl chloride. It is an oil. Boiled with dilute H_2SO_4 it forms *o*-nitro-phenyl methyl ketone and also *o*-nitro-benzoyl-acetone in smaller quantity. Conc. KOH forms a salt $CH_3CO.C(C_6H_4NO_2)K.CO_2Et$ (Gevekoht, *A.* 221, 323).

Constitution of Aceto-acetic Ether.

Some chemists adopt Frankland's formula for aceto-acetic ether, $CH_3CO.CH_2.CO_2Et$; others prefer Geuther's formula, $CH_3.C(OH):CH.CO_2Et$; while a third party, relying upon the results of Baeyer's researches into the constitution of the derivatives of indigo, consider that both formulæ are equally correct, or rather that at the moment of reaction the first may change into the second. Against Frankland's formula it is argued

(1) That the copper salt is blue or green, whereas compounds in which copper is united to carbon (*e.g.* copper acetylide) are red or yellow.

(2) That it does not account for the existence of acetyl and benzoyl derivatives.

(3) The formation of hydro-quinone dicarboxylic ether, a body containing two *hydroxyls*, by the action of sodium on di-bromo-aceto-acetic

derivative $C_6H_5.CO.C_6H_4NHBz$ [170°] (Higgin, *C. J.* 41, 133). Dilute HCl at 120° liberates the free bases, which are described as AMIDO-BENZOPHENONES (*q. v.*).

***p*-BENZOYL-PHENYL-CARBAMIC ETHER** $C_6H_5.CO.C_6H_4.NH.CO_2Et$ [189°]. Prepared by the action of chloroformic ether on *p*-amido-benzophenone (Doebner a. Weiss, *B.* 14, 1839; *A.* 210, 246). Plates. Sol. boiling alcohol, boiling acetic acid, and chloroform, insol. cold water. Decomposed by boiling KOH.

BENZOYL-PHENYL-CARBAMINE $C_6H_5.CO.C_6H_4.NC.$ *Iso-cyano-benzophenone* [119°]. From *p*-amido-benzophenone (10 g.), chloroform (8 g.), and alcoholic KOH (Doebner, *A.* 210, 246). Silky needles, volatile with steam. Sl. sol. hot water, v. sol. alcohol. Split up by acids into formic acid and amido-acetophenone.

BENZOYL-PHENYLENE-DIAMINE *v.* PHENYLENE-DIAMINE.

BENZOYL-PHENYL-DI-ETHYL-AMINE *v.* DI-ETHYL-AMIDO-BENZOPHENONE.

BENZOYL-PHENYL-DI-METHYL-AMINE *v.* DIMETHYL-AMIDO-BENZOPHENONE.

***p*-DI-BENZOYL-DI-PHENYL-THIO-UREA** $SC(NH.C_6H_4.CO.C_6H_5)_2$. [166°]. Prepared by the action of CS_2 on an alcoholic solution of *p*-amido-benzophenone in presence of a little KOH (Doebner a. Weiss, *B.* 14, 1839). Colourless plates. Sol. chloroform, sl. sol. hot alcohol, ether, benzene and CS_2; insol. water.

BENZOYL-PHENYL-METHANE is BENZOYL-PHENYL-CARBAMIC ETHER (*q. v.*).

BENZOYL-PIPER-PROPYL-ALKEÏN *v.* *Benzoyl*-OXYPROPYL-PIPERIDINE.

BENZOYL-PROPANE-CARBOXYLIC ACID *v.* PHENYL PROPYL KETONE CARBOXYLIC ACID.

a-BENZOYL-PROPIONIC ACID $C_{10}H_{10}O_3$ *i.e.* $C_6H_5.CO.CHMe.CO_2H.$ *Phenyl ethyl ketone a-carboxylic acid.* From the ether and conc. H_2SO_4, the mixture being left for 3 weeks. It is an oil and gives a reddish-brown colour with Fe_2Cl_6. Alkalis produce phenyl ethyl ketone.

Ethyl ether $CH_3.CHBz.CO_2Et.$ (227°) at 225 mm. Formed by the action of NaOEt and MeI on benzoyl-acetic ether (*q. v.*). Aromatic smelling oil. Fe_2Cl_6 gives no colour in its alcoholic solution. NaOEt forms the sodium derivative $CH_3.CNaBz.CO_2Et.$ Phosphorus pentachloride forms $C_6H_5.CCl:CMe.CO_2Et$ (Perkin a. Calman, *C. J.* 49, 156).

β-benzoyl-propionic acid $C_6H_5.CO.CH_2.CH_2.CO_2H.$ *Phenyl ethyl ketone ω-carboxylic acid.* [116°]; [114°] (Bischoff, *B.* 19, 95).

Formation.—1. By the reduction of benzoyl-acrylic acid.—2. By the action of Al_2Cl_6 ($1\frac{1}{2}$ pts.) on a mixture of succinic anhydride (1 pt.) and benzene (10 pts.). The product is shaken with water, when the acid remains dissolved in the benzene, whence it is extracted by shaking with KOH and ppg. with HCl (Burcker, *Bl.* [2] 35, 17; *A. Ch.* [5] 26, 433; Pechmann, *B.* 15, 889). 3. By oxidising its aldehyde.—4. Its chloride is formed by the action of Al_2Cl_6 upon a mixture of succinyl chloride (1 mol.) and benzene (1 mol.) (Claus, *B.* 20, 1375).—5. By heating benzoyl-isosuccinic acid above its melting-point, CO_2 being evolved (Kues a. Paal, *B.* 18, 3325).

Properties.—White prisms, v. sol. hot water. Converted by potash-fusion into benzoic and propionic acids. Reduced by sodium amalgam to γ-oxy-phenyl-butyric acid (or its lactone). $C_6H_5.CH(OH).CH_2.CH_2.CO_2H.$

Salts.—BaA'_2: needles.—AgA': sl. sol. water.

Ethyl ether. EtA'. [32°]: white crystals, turned red by heat.

Phenyl-hydrazide $C_6H_5.C(N_2HPh).CH_2.CH_2.CO_2H.$ [65°]. White silky needles, v. sol. alkalis, acids, alcohol, and benzene, sl. sol. ether.

BENZOYL-PROPIONIC ALDEHYDE $C_6H_5.CO.CH_2.CH_2.CHO.$ (245°). S.G. $\frac{0}{}$ 1·005; $\frac{18}{}$ ·998. Prepared by the action of water upon the compound of phenyl propyl ketone with CrO_2Cl_2. Oil, sol. ether and chloroform. It readily reduces $AgNO_3$, but does not combine with $NaHSO_3$. Sodium-amalgam reduces it to syrupy $C_6H_5.CH(OH).CH_2.CH_2.CH_2OH$ (c. 200°) (Burcker, *A. Ch.* [5] 26, 469; *C. R.* 94, 220).

BENZOYL-PROPIONIC-CARBOXYLIC ACID *v.* PHENYL ETHYL KETONE DI-CARBOXYLIC ACID.

BENZOYL-PYROCATECHIN *v.* DI-OXY-BENZOPHENONE.

BENZOYL PYRROL *v.* PYRROL.

Pseudo-**benzoyl-pyrrol** *v.* PYRRYL PHENYL KETONE.

BENZOYL PYRUVIC ACID $C_{10}H_8O_4$ *i.e.* $C_6H_5.CO.CH_2.CO.CO_2H.$ [156°]. Obtained by saponification of the ethyl ether. Yellowish-white prisms (from hot benzene). Strong acid. Evolves CO_2 at its melting-point.

Ethyl ether A'Et: [43°]. Prepared by adding 48 pts. of acetophenone to a cooled solution of 9·2 pts. of sodium in 150 pts. alcohol, and then 58·4 pts. of oxalic ether. The precipitated sodium compound is washed with ether, dried, dissolved in iced water, and decomposed by CO_2, when the benzoyl-pyruvic ether crystallises out; the yield is 78 p.c. of the theoretical. It crystallises from petroleum-ether in long prisms. V. sol. all ordinary solvents. Fe_2Cl_6 gives a blood-red colouration. The aqueous alcoholic solution gives with cupric acetate a light-green pp. of $(C_{12}H_{11}O_4)_2Cu$, this crystallises from hot benzene or alcohol in long green needles. By heating with dilute aqueous NaOH the ether is split up into acetophenone, oxalic acid, and alcohol. By boiling its acetic acid solution with phenyl-hydrazine it is converted into di-phenyl-pyrazol-carboxylic ether $C_3HPhN(NPh).CO_2Et.$ By cold alcoholic NH_3 it is converted into acetophenone, oxamide, and alcohol (Leyer a. Claisen, *B.* 20, 2181).

BENZOYL-QUINALDINE *v.* METHYL-QUINOLYL PHENYL KETONE.

BENZOYL-RESORCIN *v.* DI-OXY-BENZOPHENONE.

Di-benzoyl-resorcin *v.* DIOXY-PHENYLENE DI-PHENYL DIKETONE.

BENZOYL-SUCCINIC ACID. *Phenyl ethyl ketone di-carboxylic acid.* *Ethyl ether* $CO_2Et.CHBz.CH_2.CO_2Et.$ (c. 265°) at 160 mm. From sodium-benzoyl-acetic ether and chloro-acetic ether (Perkin, jun., *C. J.* 47, 274).

Properties.—Thick colourless oil. Its alcoholic solution gives a claret colour with Fe_2Cl_6. Conc. H_2SO_4 forms a yellow solution turned red by heat. NaOEt forms a solid sodium compound. Boiling baryta water decomposes it

into benzoate and succinic acids. Boiling dilute H_2SO_4 forms benzoyl-propionic acid.

Di-benzoyl-succinic acid $CO_2H.CHBz.CHBz.CO_2H$. Obtained by dissolving the ether in alcoholic KOH and treating with H_2SO_4 (Perkin, jun., *C. J.* 47, 265). The acid dissolved in alcohol gives a dark-green pp. with Fe_2Cl_6. Conc. H_2SO_4 forms a yellow solution, turned crimson by heat.

Ethyl ether $CO_2Et.CHBz.CHBz.CO_2Et$. [130°]. Formed by adding iodine to a solution of sodium benzoyl-acetic ether in dry ether (Perkin, jun., *C. J.* 47, 262). Crystals (from alcohol); sl. sol. cold alcohol, v. sol. ether. Conc. H_2SO_4 forms a colourless solution turned red, olive-green, and finally bluish-red by heat. Sodium ethylate forms $CO_2Et.CNaBz.CNaBz.CO_2Et$. In the alcoholic solution Fe_2Cl_6 gives a red colour. Boiling dilute sulphuric acid (1:2) forms an acid probably diphenyl-furfurane dicarboxylic acid, $C_{18}H_{12}O_5$, [238°], whence Ac_2O forms an anhydride $C_{18}H_{10}O_4$, [255°] (Baeyer a. Perkin, *B.* 17, 62).

β-**Benzoyl-isosuccinic acid** *v.* Phenyl ethyl ketone ω-di-carboxylic acid.

BENZOYL SULPHIDE $(C_6H_5CO)_2S$. [48°]. From BzCl and potassium thiobenzoate (Engelhardt, Latschinoff, a. Malyscheff, *Z.* 1868, 357). Waxy prisms, insol. water, v. sol. ether. Ammonia forms benzamide and ammonium thiobenzoate. Alcoholic KOH forms KOBz and KSBz. Alcoholic KSH forms KSBz.

Benzoyl disulphide $(C_6H_5CO)_2S_2$. Mol. w. 274. [128°]. Formed from $C_6H_5CO.SH$ by atmospheric oxidation of its solution in CS_2 (Cloez, *A.* 115, 27), or by treatment with iodine, Fe_2Cl_6, or HNO_3. Also, together with Bz_2S, by warming BzCl with PbS and ether (Mosling, *A.* 118, 304). When heated above its melting-point it turns violet. Prisms or tables (from CS_2), sl. sol. boiling ether and alcohol. Insol. water, NH_4Aq, and KOHAq. Alcoholic KOH forms KOBz and KSBz. Alcoholic KHS forms KSBz.

BENZOYL SULPHOCYANIDE C_6H_5COSCN. S.G. [18] 1·20. From BzCl and $Pb(SCN)_2$ in the cold (Miquel, *A. Ch.* [5] 11, 300). Pungent liquid. Decomposed by boiling water into benzamide and COS. On long standing it deposits an isomeride [160°], which is decomposed by water at 200° into NH_3, benzoic acid, and H_2S.

BENZOYL-TARTARIC ACID *v.* Tartaric acid.

BENZOYL-TEREPHTHALIC ACID *v.* Benzophenone dicarboxylic acid.

BENZOYL THIOARSENITE $C_{21}H_{15}AsS_3O_3$ *i.e.* $As(SBz)_3$. [179°]. From BzCl and As_2S_3. An ammoniacal solution gives with $HgCl_2$ a pp. of $Hg(SBz)_2$ (Rayman, *Bl.* [2] 47, 896).

BENZOYL-THIO-CARBAMIC ACID $C_8H_7NSO_2$. *Methyl ether* $Bz.NH.CO.S.Me$. [97°]. From benzoyl sulphocyanide and methyl alcohol (Miquel, *A. Ch.* [5] 11, 330). Slender needles (from dilute alcohol). Sl. sol. water, v. sol. alcohol. Water in large excess at 100° forms $BzNH_2$, methyl alcohol, H_2S, and CO_2. Salt.—$BzNNa.CO.SMe$. From the ethereal ...and MeONa.

Ethyl ether $BzNH.CO.SEt$. [74°]. From ...SCN and HO...Et; or from alcohol, BzCl, and KSCN (Lössner, ... [2] 10, 235). Long needles; v. sl. sol. water, v. sol. alcohol. Boiling KOHAq forms KOBz, KSCN, alcohol, CO_2, NH_3, and H_2S. Heated alone it gives benzonitrile, CO, and mercaptan. Salt.—$BzNK.CO.SEt$: needles.

BENZOYL THIOCYANATE *v.* Benzoyl sulphocyanide.

BENZOYL-THIO-UREA *v.* Thio-urea.

BENZOYL-THYMOL *v.* Thymol.

BENZOYL-TOLUENE-SULPHAMIDE *v.* Toluene sulphonic acid.

BENZOYL-TOLUIDE *v.* Toluidine.

BENZOYL-TOLUIDINE-IMIDE-CHLORIDE *v.* ω-Chloro-benzylidene-toluidene.

BENZOYL-TOLYLENE-DIAMINE *v.* Tolylene-diamine.

BENZOYL-TROPEÏNE *v.* Tropin.

BENZOYL-UREA *v.* Urea.

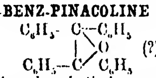
BENZOYL-URITIC ACID *v.* Phenyl tolyl ketone di-carboxylic acid.

α-**BENZOYL-VALERIC ETHER** *v.* *Propyl-*Benzoyl-acetic ether.

BENZOYL-XYLENE *v.* Phenyl xylyl ketone.

BENZOYL-XYLIDE *v.* Xylidine.

(*α*)-**BENZ-PINACOLINE** $C_{26}H_{20}O$ *i.e.*



(?) [204°].

Tetra-phenyl-ethylene oxide.

Formation.—1. Together with the (*β*)-modification by boiling a 5 p.c. alcoholic solution of benzophenone with zinc and HCl (Thörner a. Zincke, *B.* 11, 65).—2. Together with benzpinacone by heating an alcoholic solution of benzophenone with zinc and H_2SO_4 (Thörner a. Zincke, *B.* 11, 1396).—3. By the action of zinc-dust on an ethereal solution of acetyl chloride (1 mol.) and benzophenone (1 mol.). If the acetyl chloride is used in excess the (*α*)-benz-pinacoline first formed is converted into the (*β*)-benz-pinacoline (Paal, *B.* 17, 911).—4. By the oxidation of tetra-phenyl-ethylene with chromic mixture (Behr, *B.* 5, 277).

Properties.—Needles. Almost insoluble in cold alcohol and in cold acetic acid.

Reactions.—1. By acetyl chloride, HCl or H_2SO_4, it is converted into the (*β*)-modification. 2. By heating with soda lime it gives a hydrocarbon [244°] which is possibly tetraphenyl-ethylene.—3. By CrO_3 and acetic acid it is oxidised to benzophenone.

(*β*)-**Benz-pinacoline** $(C_6H_5)_3C.CO.C_6H_5$ [179°] (T. a. Z.); [182°] (Zagumenny).

Formation.—By boiling a concentrated solution of benzophenone in alcohol with zinc and HCl for 20 hours (Thörner a. Zincke, *B.* 10, 1473; 11, 65).—2. From benzpinacone and AcCl or BzCl (Linnemann, *A.* 133, 28).—3. From benzpinacone and dilute H_2SO_4 or HCl at 200°. It is even slowly formed by repeatedly recrystallising benzpinacone from hot alcohol (Z.).—4. From (*α*)-benzpinacoline by heating with AcCl, HCl, or H_2SO_4.

Preparation.—HClAq is added to a saturated solution of benzpinacone in HOAc until a turbidity appears. The mixture is boiled 45 minutes, with gradual addition of HClAq (Zagumenny, *Bl.* [2] 34, 329; 35, 560).

ether. This indicates the presence of *hydroxyl* in di-bromo-aceto-acetic ether.

(4) The action of ammonia, and especially of di-ethylamine.

In favour of Frankland's formula may be noted the compounds with $NaHSO_3$, phenyl-hydrazine, and hydroxylamine.

The action of sodium upon aceto-acetic ether would be represented by Frankland's formula, thus:

$$CH_3.CO.CH_2.CO_2Et + Na = CH_3.CO.CNaH.CO_2Et + H.$$

Ethyl iodide converts the product into ethyl-aceto-acetic ether:

$$CH_3.CO.CNaH.CO_2Et + EtI = CH_3.CO.CEtH.CO_2Et + NaI$$

These two reactions may be repeated upon the ethyl-aceto-acetic ether:

$$CH_3.CO.CEtH.CO_2Et + Na = CH_3.CO.CEtNa.CO_2Et + H$$
$$CH_3.CO.CEtNa.CO_2Et + EtI = CH_3.CO.CEt_2.CO_2Et + NaI.$$

Adopting Geuther's formula, the four equations become:

$$CH_3.C(OH):CH.CO_2Et + Na = CH_3.C(ONa):CH.CO_2Et + H$$
$$CH_3.C(ONa):CH.CO_2Et + EtI = CH_3.C(OEt):CH.CO_2Et + NaI$$
$$CH_3.C(OEt):CH.CO_2Et + Na = CH_3.C(OEt):CNa.CO_2Et + H$$
$$CH_3.C(OEt):CNa.CO_2Et + EtI = CH_3.C(OEt):CEt.CO_2Et + NaI$$

It will be seen that the third and fourth equations are similar to the first and second on Frankland's hypothesis, but different in kind to the first and second if Geuther's hypothesis be accepted. Such a difference is not borne out by experiment. Thus if it be held that the action of sodium upon aceto-acetic ether depends upon its affinity for oxygen, the third equation presents a difficulty. And if we suppose that, owing to some intra-molecular change, the third equation ought to be written thus:

$$CH_3.C(OEt):CH.CO_2Et + Na = CH_3.C(ONa):CEt.CO_2Et + H$$

then by the action of acetic acid on the product we ought to get an ether $CH_3.C(OH):CEt.CO_2Et$ isomeric, not identical, with ethyl-aceto-acetic ether, $CH_3.C(OEt):CH.CO_2Et$; but the two ethers are found to be identical (James, *C. J.* 47, 1). Inasmuch as the change of $CH_3.C(OH):CEt.CO_2Et$ into $CH_3.C(OEt):CH.CO_2Et$ would be contrary to all analogy, it is necessary, if we adopt Geuther's formula, to assume that the mode of formation of di-ethyl-aceto-acetic ether is something very different from that of ethyl-aceto-acetic ether. Again Geuther's formula would make methyl-ethyl-aceto-acetic ether, $CH_3.C(OEt):CMe.CO_2Et$ and ethyl-methyl-aceto-acetic ether, $CH_3.C(OMe):CEt.CO_2Et$ isomeric, yet this does not appear to be the case (James).

It may be said that there is some improbability in the assumption required by Frankland's formula, of direct union between sodium and carbon, but such a union is known to occur in sodium acetylide and sodium ethide, and it is very probable in many cases, such as sodio-malonic ether, sodium nitro-ethane, and sodic barbiturate. In order that hydrogen attached to carbon may be displaceable by metals, it is necessary that very powerful chlorous groups should also be attached to the carbon, such as the nitroxyl in nitro-ethane. One carbonyl, CO, is not sufficient to produce an acid, but two are. Thus the hydrogen in the group $CO.CH_2.CO$ is displaceable by metals, as in barbituric acid,

$$CO\left\langle\begin{matrix} NH.CO \\ NH.CO \end{matrix}\right\rangle CH_2.$$

These considerations account for the acidity of aceto-acetic ether, if we assume Frankland's formula $CH_3.CO.CH_2.CO.OH$.

Although the existence of acetyl-aceto-acetic ether favours Geuther's hypothesis, yet the fact that this body is a strong acid is wholly opposed to that view, and is very much better explained by the formula $CH_3.CO.CH(CO.CH_3).CO.OEt$, since if two carbonyls can make the group CH_2 acid, *à fortiori* three carbonyls can have a similar effect.

The formation of ethyl and di-ethyl-acetone from ethyl-aceto-acetic ether and di-ethyl-aceto-acetic ether respectively cannot be explained on Geuther's hypothesis.

If, therefore, we have to choose between one formula and the other, the balance of evidence would indicate $CH_3.CO.CH_2.CO_2Et$.

Methyl aceto-acetate $C_5H_8O_3$ *i.e.* $CH_2Ac.CO_2Me$ (170° cor.) S.G. $\frac{0}{}$ 1·037 (Brandes, *J.Z.* 3, 25). From sodium and methyl acetate. Gives a cherry-red colour with Fe_2Cl_6. Boiled with acids or strong bases it gives CO_2, acetone, and MeOH.

Salts.—$CH_3.CO.CHNa.CO_2Me$. Sl. sol. ether. —$Cu(C_5H_7O_3)_2 2aq$. Separates on adding cupric acetate and baryta water to the ether as pale green crystals, insoluble in alcohol.

Iso-butyl aceto-acetate $C_8H_{14}O_3$ *i.e.* $CH_2Ac.CO_2C_4H_9$ (202°-206°) S.G. $\frac{0}{}$ ·979; $\frac{22}{4}$ ·932. From iso-butyl acetate and sodium.

Iso-amyl aceto-acetate $C_9H_{16}O_3$ *i.e.* $CH_2Ac.CO_2C_5H_{11}$ (223°) S.G. $\frac{10}{17.5}$ ·954. From iso-amyl acetate and Na (Conrad, *A.* 186, 228). Converted by Cl into an oily di-chloro-derivative (Conrad, *A.* 186, 243) and by NH_3 into the imide of aceto-acetate of iso-amyl [190°-195°] (Collie, *A.* 226, 319).

ALKYLATED ACETO-ACETIC ETHERS.

Sodium aceto-acetic ether is converted by alkyl iodides into mono-alkyl aceto-acetic ethers, $CH_3.CO.CXH.CO_2Et$. The sodium derivatives of these are in like manner converted by alkyl iodides into di-alkyl-aceto-acetic ethers, $CH_3.CO.CXY.CO_2Et$. Such ethers are of great service in organic syntheses, for they are split up by weak alkalis into carbonic acid and mono- or di-alkyl acetones: $CH_3.CO.CXY.CO_2Et + 2KOH = CH_3.CO.CXYH + HOEt + K_2CO_3$, and by strong potash into mono- or di-alkyl-acetic acid and acetic acid: $CH_3.CO.CXY.CO_2Et + 2KOH = CH_3.CO_2K + HCXY.CO_2K + HOEt$.

In practice the ketonic and acetic decompositions both occur, at the same time, but the acetic decomposition increases with the concentration of the alkali (Wislicenus, *A.* 206, 308).

Preparation.—The alkyl-aceto-acetic ethers are prepared by dissolving the calculated quantity of sodium in 10 times its weight of absolute alcohol, cooling, adding the aceto-acetic ether and then the alkyl iodide until the liquid, which may be warmed, if necessary, is neutral to litmus. The greater part of the alcohol is then distilled off and water is added. This dissolves the NaI and the new ether rises as an oil and is fractionated (Conrad a. Limpach, *A.* 192, 154).

A. WITH ONE MONOVALENT RADICLE.

Methyl-aceto-acetic Acid $C_5H_8O_3$ *i.e.* $CH_3.CO.CHMe.CO_2H$. A thick liquid which splits up on warming into CO_2 and methyl ethyl ketone (Ceresole, *B.* 15, 1874). Its barium salt is soluble and gives a violet colour with Fe_2Cl_6. Nitrous acid forms iso-nitroso-methyl-ethyl-ketone.

Methyl Ether $CH_3.CO.CHMe.CO_2Me$

(177·4° cor.) S.G. $\frac{?}{?}$ 1·020 (Brandes, *Z.* 1866, 458). From sodium aceto-acetate of methyl and MeI. Smells like mint. Gives a violet-red colour with Fe_2Cl_6.

Ethyl Ether $CH_3.CO.CHMe.CO_2Et$ (186·8° cor.) (Geuther, *Z.* 1866, 5). S.G. $\frac{?}{}$ 1·009. Gives a deep blue colour with Fe_2Cl_6.

Reactions.—1. *Sodium amalgam* gives an oxy-valeric acid $CH_3CH(OH).CHMe.CO_2H$.—2. *Potash* forms methyl-ethyl ketone, alcohol and K_2CO_3.—3. PCl_5 gives chloro-methyl-crotonic acid [69·5°] (206°) (Rücker), chloro-methyl-aceto-acetic ether, $C_7H_{11}ClO_3$ (180°) S.G. $\frac{15}{}$ 1·093, smelling of peppermint, and di-chloro-methyl-aceto-acetic ether (210°–220°) S.G. $\frac{11}{}$ 1·225 (Isbert, *A.* 234, 188).—4. Sodium and *cyanogen chloride* form *cyano-methyl-aceto-acetic ether* $CAcMeCy.CO_2Et$ (c. 93°) at 20 mm. S.G. $\frac{22}{}$ ·996. It is a colourless liquid insol. water and alkalis (Held, *C. R.* 95, 522; *Bl.* [2] 41, 330).

Acetyl derivative $C_9H_{14}O_4$ *i.e.* $CMeAc_2CO_2Et$. *Methyl-diacetyl-acetic ether* (205°–220°). From methyl-aceto-acetic ether in ethereal solution and AcCl (James, *A.* 226, 219, *C. J.* 47, 1). Sl. sol. water. Coloured raspberry red by Fe_2Cl_6. Does not pp. cupric acetate, even on addition of dilute NaOH.

Ethyl-aceto-acetic acid.

Methyl ether $CH_3.CO.CEtH.CO_2Me$ (189·7° cor.) S.G. $\frac{14}{}$ ·995 (Brandes, *Z.* 1866, 457), Fe_2Cl_6 gives deep violet colour. Conc. NH_3 forms an oil $C_7H_{13}NO_2$, the imide of ethyl-aceto-acetate of methyl insoluble in water, and also silky needles [83°] of a soluble amide (probably $C_6H_{11}NO_2$ see below) (Brandes, *Z.* 1866, 457).

Ethyl ether $C_8H_{14}O_3$ *i.e.* $CAcEtH.CO_2Et$ (198° cor.) S.G. $\frac{12}{}$ ·998 (G.); $\frac{14}{4}$ ·983 (F. D.) (Geuther, *Ar. Ph.* [2] 116, 97; Frankland a. Duppa, *C. J.* [2] 4, 396; Wislicenus, *A.* 186, 187).

Preparation.—Aceto-acetic ether is dissolved in benzene and four-fifths of the calculated quantity of sodium added, then EtI, and the product rectified. The aceto-acetic ether recovered is treated with the remaining fifth of the sodium. Yield 70 per cent. (Wedel, *A.* 219, 100).

Properties.—An oil. Coloured blue by Fe_2Cl_6.

Reactions.—1. Reduced by *sodium amalgam* to an oxy-hexoic acid, $CH_3.CH(OH).CHEt.CO_2H$. 2. Boiled with *baryta* or weak alcoholic KOH, it gives methyl propyl ketone.—3. Boiled with conc. alcoholic KOH, or heated with dry NaOEt, it gives *n*-butyric acid and acetic acid, or their ethers.—4. Treated with NaOEt and *cyanogen chloride* it forms *cyano-ethyl-aceto-acetic ether*, $CH_3.CO.CEtCy.CO_2Et$ (c. 105°) at 20 mm. S.G. $\frac{22}{}$ ·976. A colourless liquid with agreeable odour. Insol. in water or alkaline solutions, miscible with alcohol or ether (Held, *C. R.* 98, 522, *Bl.* [2] 41, 330).—5. *Bromine* acting on an ethereal solution forms mono- di- and tri- BROMO-ETHYL-ACETO-ACETIC ETHER (*q. v.*).—6. PCl_5 gives mono- and di- CHLORO-ETHYL-ACETO-ACETIC ETHER, and only one CHLORO-ETHYL-CROTONIC ACID (*q. v.*) (Isbert, *A.* 234, 183).—7. *Benzoic aldehyde* and HCl form the same benzylidene-ethyl-aceto-acetic ether or cinnamoyl-ethyl-acetic ether, $Ph.CH:CH.CO.CHEt.CO_2Et$ (210°) at 22 mm. Converted by NaOEt and EtI into cinnamoyl-di-ethyl-acetic ether.—8. Conc. aqueous *ammonia* forms two amides, one soluble in water, $C_6H_{11}NO_2$, the other insoluble, $C_6H_{13}NO_2$. They are formed in equi-molecular quantities; the oily insoluble amide crystallises when cooled. On distilling the soluble amide does not pass over with steam.

Insoluble amide $C_6H_{13}NO_2$ imide of ethyl-aceto-acetic ether $CH_3.C(NH).CHEt.CO_2Et$ or $CH_3.C(NH_2):CEt.CO_2Et$ [59·5°]. Monoclinic tablets (from alcohol), smelling of peppermint. Decomposed by water, or dilute acids, into NH_3 and ethyl-aceto-acetic ether (Geuther, *Z.* 1871, 247).

Soluble amide $C_6H_{11}NO_2$ *i.e.* $CAcHEt.CONH_2$ [90°]. Needles (from water, alcohol, or ether). May be sublimed. May be obtained from the preceding body by heating with water at 135°. On dry distillation it gives NH_3, CO_2 and methyl propyl ketone. The latter body is also formed by heating it with water at 200°, with boiling aqueous HCl, with $CaCl_2$, $ZnCl_2$, P_2O_5, or PCl_5 (Isbert takes it to be di-ethyl ketone). Heated with dry KOH at 100° it forms butyric and acetic acids (Isbert, *A.* 234, 170).

Salts.—$CH_3.CO.CNaEt.CO_2Et$. Formed by adding sodium to a solution of ethyl-aceto-acetic ether in dry ether or benzene (3 or 4 vols.) (J. W. James, *C. J.* 47, 1). Also by shaking an ethereal solution of the ether with perfectly dry NaOH (Elion, *R.* 3, 234). It is amorphous. V. sol. ether. A little water added to its ethereal solution forms a pp. of $CH_3.CO.CNaEt.CO_2Et$ aq, insol. ether or benzene, but sol. water or alcohol. Acetic acid re-converts the sodium salt into ethyl-aceto-acetic ether (v. *constitution* of ACETO-ACETIC ETHER).

Ethyl aceto-acetic ether forms no copper compound. This is thought to favour the formula $CH_3.C(OEt):CH.CO_2Et$.

Iso-amyl ether $CH_3.CO.CHEt.CO_2C_5H_{11}$ (233°–236°) S.G. $\frac{20}{17.5}$ ·937 gives no colour with Fe_2Cl_6 (Conrad, *A.* 186, 228).

Acetyl derivative $CH_3.CO.CAcEt.CO_2Et$. *Ethyl-di-acetyl-acetic ether* (c. 230°); (144°–150°) at 50 mm. S.G. $\frac{15}{}$ 1·034. From $CH_3.CO.CNaEt.CO_2Et$ and AcCl (Elion, *R.* 3, 265). Liquid. Insol. KOHAq. Gives no colour with Fe_2Cl_6. Alcoholic NH_3 converts it into acetamide and $CH_3.CO.CHEt.CO_2Et$.

Allyl-aceto-acetic Ether $C_9H_{14}O_3$ *i.e.* $CH_3.CO.CH(C_3H_5).CO_2Et$ (206°) (Zeidler, *A.* 187, 33) (214° cor.) at 720 mm. (Perkin, *C. J.* 45, 540). S.G. $\frac{20}{17.5}$ ·982 (*Z.*); $\frac{15}{15}$ ·993; $\frac{25}{25}$ ·985 (P.). From sodium aceto-acetic ether and allyl iodide (*Z.*; Wolff, *A.* 201, 46). From aceto-acetic ether, allyl iodide, and zinc, di-allyl-aceto-acetic ether being also formed (O. Hofmann, *A.* 201, 77).

Reactions.—1. Fe_2Cl_6 gives a crimson colour. 2. Boiling alcoholic KOH forms CO_2 and allyl-acetone.—3. Dry NaOEt at 150°–160° gives ethyl acetate and allyl-acetate.—4. *Sodium amalgam* forms an oxy-heptenoic acid,

$$CH_3.C(OH)H.CH(C_3H_5)CO_2H.$$

Propyl-aceto-acetic Ether $C_9H_{16}O_3$ *i.e.* $CH_3.CO.CHPr.CO_2Et$ (209°) S.G. $\frac{0}{}$ ·981. From aceto-acetic ether (153g.) by adding first a solution of sodium (27g.) in dry alcohol (270g.) and then PrI (206g.) (Burton, *Am.* 3, 385). Decomposed by aqueous KOH into CO_2, alcohol, and methyl butyl ketone.

Iso-propyl-aceto-acetic Ether $C_9H_{16}O_3$ *i.e.* $CH_3.CO.CPrH.CO_2Et$ (201°) at 758 mm. S.G. $\frac{?}{}$ ·880. From sodium aceto-acetic ether and iso-propyl iodide (Frankland a. Duppa, *A.* 145, 78).

Coloured pale reddish-violet by Fe_2Cl_6 (Demarçay, *Bl.* 27, 224).

Iso-butyl-aceto-acetic Ether $C_{10}H_{18}O_3$ *i.e.* $Pr.CH_2CHAc.CO_2Et$ (218°) S.G. $\frac{17.5}{}$ ·951. From sodium aceto-acetic ether and iso-butyl iodide (Rohn, *A.* 190, 306). Decomposed by baryta giving methyl iso-amyl ketone and iso-butyl-acetic (hexoic) acid.

Heptyl-aceto-acetic Ether $C_{13}H_{24}O_3$ *i.e.* $CH_3.CO.CH(C_7H_{15}).CO_2Et$ (272°) S.G. $\frac{17.7}{17.7}$ ·9324. From sodium aceto-acetic ether and heptyl iodide (Jourdan, *A.* 200, 105). Colourless oil. Decomposed by dilute alkalis into methyl octyl ketone and CO_2; and by conc. alkalis into acetic and *n*-ennoic acids.

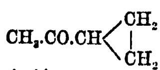
Secondary Heptyl-aceto-acetic Ether (250°–260°). Prepared similarly from secondary heptyl iodide (Venable, *B.* 13, 1651).

Octyl-aceto-acetic Ether $C_{14}H_{26}O_3$ *i.e.* $CH_3.CO.C(C_8H_{17})H.CO_2Et$ (281°) S.G. $\frac{18.5}{17.5}$ ·9354. From octyl iodide and sodium aceto-acetic ether (Guthzeit, *A.* 204, 1). Decomposed by alcoholic KOH into methyl ennyl ketone and decoic acid.

Benzyl-aceto-acetic Ether $C_{13}H_{16}O_3$ *i.e.* $CH_3.CO.CH(CH_2Ph)CO_2Et$ (276°) S.G. $\frac{15.5}{16.5}$ 1·036. From sodium aceto-acetic ether and benzyl chloride (Ehrlich, *B.* 7, 690; *A.* 187, 12; Conrad, *B.* 11, 1056). Sodium amalgam gives exo-oxy-phenyl-valeric acid $CH_3.CH(OH).CH(CH_2Ph).CO_2Et$. Alcoholic KOH forms phenyl-ethyl methyl ketone.

B. With two Di-valent Radicles:

Ethylene-aceto-acetic Acid.
$CH_3.CO.C(C_2H_4).CO_2H$. From the ether by saponification. Liquid. Decomposed by heat or by dilute acids into tri-methylene methyl ketone

 and CO_2.

Salt.—AgA'.

Ethyl ether.—EtA' (193°–195°). From aceto-acetic ether (26g.) by adding a solution of sodium (5g.) in alcohol followed by ethylene bromide (38g.) The liquid is boiled for eight hours, filtered, and distilled. The residue is boiled for twelve hours longer with a solution of sodium (5g.) in alcohol, evaporated, and treated with water. The ether is extracted by ether and dried over K_2CO_3 (W. H. Perkin, jun., *C.J.* 47, 834; *B.* 16, 2136; 19, 1247). It reacts with phenyl-hydrazine, forming an oil.

Ethylidene-aceto-acetic Ether.
$CH_3.CH:CAc.CO_2Et$ (210°–212°) S.G. $\frac{15}{}$ 1·023 By passing HCl into aldehyde (1 pt.) mixed with aceto-acetic ether (3 pts.) (L. Claisen a. F. H. Matthews, *A.* 218, 172; Claisen, *B.* 14, 345).

Pungent ethereal oil. Miscible with H_2SO_4.

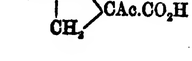
Reactions.—1. Hot potash decomposes it, forming aldehyde.—2. Combines with bromine.

Tri-chloro-ethylidene-aceto-acetic Ether.
$CCl_3.CH:CAc.CO_2Et$. S.G. $\frac{15}{}$ 1·342

From chloral, aceto-acetic ether and Ac_2O at 160°. (Claisen a. Matthews, *A.* 218, 175).

Thick oil. Decomposed by heat.

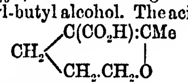
Propylene-aceto-acetic Acid.



From the ether by saponification. Oil. Forms an amorphous silver salt, AgA'.

Ethyl ether (210°–215°) at 720 mm. Aceto-acetic ether (26g.) is heated with sodium (4·6g.), dissolved in dry alcohol and propylene bromide (40g.) at 100°. After two days the tubes are opened and a fresh quantity of alcoholic NaOEt (from 4·6g. sodium) is added, and the tubes heated again at 100° (Perkin, jun., *B.* 17, 1443).

Tri-methylene Bromide acts on aceto-acetic ether in presence of NaOEt, but the product $C_9H_{14}O_3$ (V.D. 6·21) is not tri-methylene-aceto-acetic ether, for its boiling point (223°) and molecular magnetic rotation, 10·195, are both too high, and it does not react with phenyl-hydrazine. It is, however, the ether of a crystalline acid which splits up on distillation into CO_2 and $C_6H_{10}O$, and on boiling with water into CO_2 and acetyl-butyl alcohol. The acid is probably



(Perkin, jun., *B.* 16, 208, 1789; 19, 1247, 2557).

Iso-butylidene-aceto-acetic Ether
$(CH_3)_2CH.CH:CAc.CO_2Et$ (219°–222°).
From isobutyric aldehyde, aceto-acetic ether and HCl (Claisen a. Matthews, *A.* 218, 174).

Liquid smelling of peppermint.

Iso-amylidene-aceto-acetic Ether.
$(CH_3)_2CH.CH_2.CH:CAc.CO_2Et$
(237°–241°) S.G. $\frac{15}{}$ ·961. From valeric aldehyde, aceto-acetic ether and HCl (Claisen a. Matthews, *A.* 218, 174).

Benzylidene-aceto-acetic Ether
$Ph.CH:CAc.CO_2Et$ (α-aceto-cinnamic ether), [60°] (180°–182°) at 17 mm. (295°–297°) at 760 mm. From aceto-acetic ether, benzoic aldehyde and gaseous HCl at 0°. (Claisen a. Matthews, *A.* 218, 177) 4 or 6 sided tables (from alcohol); trimetric, a : b : c = ·447 : 1 : ·962. Colourless oil, solidifying very slowly. V. sol. chloroform, m. sol. cold alcohol, ether, glacial acetic acid or CS_2, v. sl. sol. benzoline. Insoluble in aqueous KOH. H_2SO_4 forms a bright yellow solution which, on warming, becomes very dark red. On pouring this solution into water a white pp. is formed, and on adding NaOH this dissolves, forming a violet solution.

Reactions.—Bromine in ether forms a di-bromide [97°]. This forms short needles (from benzoline).

Theory of the Process.—Benzoic aldehyde probably first combines with HCl forming Ph.CH(OH)Cl, and this reacts with aceto-acetic ether thus:

$$Ph.CHCl(OH) + CH_2Ac.CO_2Et = H_2O + Ph.CHCl.CHAc.CO_2Et.$$

Two compounds of this formula may be isolated before distillation, one forms prisms [41°], the other small rhombohedra or triclinic tables [72°] (both from benzoline). They are both unstable, giving off HCl. One of them has probably the formula $Ph.CHCl.CHAc.CO_2Et$ and decomposes into HCl and $Ph.CH:CAc.CO_2Et$, which recombines with HCl forming the other $Ph.CH_2.CClAc.CO_2Et$. On distillation both probably give HCl and benzylidene-aceto-acetic ether.

Benzylidene-ethyl-aceto-acetic Ether
$Ph.CH:CH.CO.CHEt.CO_2Et$
(205°–220°) at 22 mm. (Cinnamoyl-ethyl-acetic ether). From benzoic aldehyde, ethyl-aceto-

acetic ether, and HCl. Yield small (Claisen a. Matthews, *A.* 218, 184).

Benzylidene-di-ethyl-aceto-acetic Ether

$Ph.CH:CH.CO.CEt_2.CO_2Et$

[101°-102°]. *Formation.*—(1) From the above, NaOEt, and EtI.—(2) From benzoic aldehyde, di-ethyl-aceto-acetic ether, and HCl (C.M.). Triclinic prisms (from benzoline). V. sol. ether or chloroform, m. sol. cold alcohol or benzoline. *Dibromide* [55°].

Furfural-aceto-acetic Ether

$(C_5H_4O)''CAc.CO_2Et$

[62·5°]. (189°) at 30 mm. From furfur-aldehyde, aceto-acetic ether, and Ac_2O at 160°. (Claisen a. Matthews, *A.* 218, 176.) Trimetric crystals, a : b : c = ·439 : 1 : ·465. V. sol. alcohol, glacial acetic acid, chloroform, and benzene. M. sol. ether, sl. sol. benzoline.

C. WITH TWO MONOVALENT RADICLES.

Di-methyl-aceto-acetic Acid

$C_6H_{10}O_3$ *i.e.* $CH_3.CO.CMe_2.CO_2H$.

From the ether by dissolving in cold dilute ($2\frac{1}{2}$ per cent.) aqueous KOH, setting aside for a day or two, then acidifying with H_2SO_4, extracting with ether, evaporating the ether, and triturating with $BaCO_3$. The crystalline barium salt, BaA'_2, is decomposed by dilute H_2SO_4 (Ceresole, *B.* 15, 1871). Very hygroscopic crystals, which slowly split up into CO_2 and methyl isopropyl ketone. The barium salt gives a brown colour or pp. with Fe_2Cl_6. It reduces boiling silver nitrate.

Ethyl Ether

$C_8H_{14}O_3$ *i.e.* $CH_3.CO.CMe_2.CO_2Et$

(184°) S.G. $\frac{16}{}$ ·991. From sodium methyl-aceto-acetic ether and MeI (Frankland a. Duppa, *A.* 138, 328). Potash or baryta splits it up into alcohol, CO_2, and methyl iso-propyl ketone.

Methyl-ethyl-aceto-acetic Ether

$CH_3.CO.CMeEt.CO_2Et$

(196° uncor.) (*J.*) (201° i. V.) (Wislicenus, *A.* 219, 308). S.G. $\frac{22}{17.5}$ ·947. From sodium ethyl-aceto-acetic ether and MeI (Saur, *A.* 188, 257); or sodium methyl-aceto-acetic ether and EtI (J. W. James, *A.* 226, 209; *C. J.* 47, 1). Oil. Fe_2Cl_6 gives a violet colour. Distilled with dry NaOEt it gives ethyl acetate and ethyl methyl-ethyl-acetate (or valerate).

Methyl-allyl-aceto-acetic Ether

$C_{10}H_{16}O_3$ *i.e.* $CH_3.CO.CMe(C_3H_5)CO_2Et$

(c. 209°-211°). From allyl-aceto-acetic ether, MeI, and NaOEt (James, *C. J.* 47, 3). Pleasant-smelling oil, miscible with alcohol, ether, or benzene. Fe_2Cl_6 gives no colour. The same body may be got from methyl-aceto-acetic ether, allyl iodide, and NaOEt.

Methyl-propyl-aceto-acetic Ether

$C_{10}H_{18}O_3$ *i.e.* $CH_3.CO.CMePr.CO_2Et$

(214°) (L.K.); (216°) (J.). S.G. $\frac{15}{}$ ·959 (L.K.); $\frac{17}{}$ ·9575 (J.). From methyl-aceto-acetic ether, NaOEt, and PrI (Liebermann a. Kleemann, *B.* 17, 918) or from propyl-aceto-acetic ether, NaOEt, and MeI (E. J. Jones, *A.* 226, 287).

Di-ethyl-aceto-acetic acid

$CH_3.CO.C(C_2H_5)_2.CO_2H$.

Thick colourless liquid. Sl. sol. water.

Preparation.—Di-ethyl-acet-acetic ether is left in the cold for several weeks with 10 p.c. aqueous KOH. After removing the unaltered ether, the product is acidified and extracted with ether, and the acid purified by conversion into the barium salt, acidifying the latter, and again extracting with ether.

Reactions.—It decomposes very slowly in the cold, but on heating to 60° it rapidly evolves CO_2, forming di-ethyl-acetone. The latter body is also formed by distilling the barium salt.

Salts.—A'Na; easily soluble white microscopic crystals.—A'_2Ba 2aq; transparent prisms, rotates on water (Ceresole, *B.* 16, 830).

Ethyl ether $C_{10}H_{18}O_3$ *i.e.* $CH_3.CO.CEt_2.CO_2Et$ (218°). S.G. $\frac{20}{}$ ·974. From sodium ethyl-aceto-acetic ether and EtI (Frankland a. Duppa, *A.* 138, 211; James, *A.* 226, 205). From $Cl.CO_2Et$, Na, and EtI (Geuther a. Matthey, *J. pr.* [2] 6, 160).

Reactions.—1. With hot aqueous *baryta* it gives di-ethyl-acetone.—2. Distilled with dry NaOEt it gives di-ethyl-acetic (hexoic) ether, acetic acid, and sodic di-ethyl-acetate.—3. PCl_5 gives mono- and di-chloro-di-ethyl-aceto-acetic ether and chloro-ethyl-crotonic ether (James, *A.* 231, 235).—4. With *benzoic aldehyde* and HCl gas it forms some $C_6H_5.CH:CH.CO.CEt_2.CO_2Et$, cinnamoyl-di-ethyl-acetic ether. Crystals, [102°], (200°-205°) at 3 mm. Easily soluble in ether and chloroform, slightly in cold alcohol and in light petroleum (Matthews, *C. J.* 43, 205). Bromine in chloroform forms a di-bromide, [55°]. Prisms v. sol. alcohol and light petroleum.

Di-allyl-aceto-acetic Ether

$C_{12}H_{18}O_3$ *i.e.* $CH_3.CO.C(C_3H_5)_2CO_2Et$

(240°). S.G. $\frac{25}{17.5}$ ·948. From sodium allyl-aceto-acetic ether and allyl bromide (Wolff, *A.* 201, 45). From aceto-acetic ether, allyl iodide, and zinc (O. Hofmann, *A.* 201, 77). Colourless oil, with faint peculiar odour. Insol. water, sol. alcohol, ether, or benzene. Boiling conc. KOHAq forms di-allyl-acetone, or methyl heptinyl ketone, and di-allyl-acetic acid.

Di-propyl-aceto-acetic Ether $C_{12}H_{22}O_3$ *i.e.* $CH_3.CO.CPr_2.CO_2Et$ (236°). S.G. $\frac{0}{4}$ ·9585. From sodium propyl-aceto-acetic ether and PrI (Burton, *Am.* 3, 386). Alkalis split it up, giving di-propyl-aceto-acetic ether and di-propyl-acetone or methyl heptyl ketone.

Di-isobutyl-aceto-acetic Ether $C_{14}H_{26}O_3$ *i.e.* $(PrCH_2)_2CAc.CO_2Et$ (250°-253°). S.G. $\frac{10}{}$ ·947. From sodium isobutyl-aceto-acetic ether and isobutyl iodide (Mixter, *B.* 7, 500).

Di-*n*-heptyl-aceto-acetic Ether

$C_{20}H_{38}O_3$ *i.e.* $CH_3CO.C(C_7H_{15})_2CO_2Et$

(332°) S.G. $\frac{17.5}{17.5}$ ·891. Formed together with di-heptyl-acetic ether and methyl octyl ketone by heating sodium heptyl-aceto-acetic ether with heptyl iodide and dry alcohol for a long time (Jourdan, *A.* 200, 112). Decomposed by dilute alkalis into CO_2 and methyl pentadecyl ketone, and by concentrated alkalis into acetic and di-heptyl-acetic (hexadecoic) acids.

Di-octyl-aceto-acetic Ether

$C_{22}H_{42}O_3$ *i.e.* $CH_3.CO.C(C_8H_{17})_2.CO_2Et$

(264°) at 90 mm. (340°-342°) at 760 mm. From octyl-aceto-acetic ether, NaOEt, and octyl iodide (Guthzeit, *A.* 204, 9). Decomposed by alkalis into di-octyl-acetone (methyl heptadecyl ketone) and di-octyl-acetic (heptadecoic) acid.

Benzyl-methyl-aceto-acetic Acid

$C_{11}H_{14}O_3$ *i.e.* $CH_3.CO.CMe(CH_2Ph).CO_2H$

[34°] (275°). From the ether by saponification Sl. sol. cold water. *Salt*: AgA'.

Ethyl ether—EtA' (287°). S.G. $\frac{15}{15}$ 1·046. Prepared by action of MeI on a mixture of benzyl-aceto-acetic acid and sodium ethylate (Conrad, *B.* 11, 1055).

Benzyl ether—$PhCH_2A'$ (53°?). Methyl hydro-cinnamein. Liquid.

Benzyl-ethyl-aceto-acetic Ether

$CH_3.CO.CEt(CH_2Ph).CO_2Et$

(296°). Colourless liquid.

Di-benzyl-aceto-acetic Ether

$CH_3.CO.C(CH_2Ph)_2.CO_2Et.$

From sodium benzyl-aceto-acetic ether and benzyl chloride (Ehrlich, *A.* 187, 24). Thick non-volatile liquid.

OTHER DERIVATIVES of aceto-acetic acid will be described as acetyl derivatives, *e.g.* ACETYL-GLUTARIC ETHER, ACETYL-SUCCINIC ETHER, &c. See also OXY-ACETO-ACETIC ETHER, OXY-DI-ETHYL-ACETO-ACETIC ETHER, OXY-DI-METHYL-ACETO-ACETIC ETHER.

For analogous acids see PROPIONYL-PROPIONIC ACID, VALERYL-VALERIC ACID.

ACETO-BENZOYL-BENZOIC ANHYDRIDE *v.* BENZOYL-BENZOIC ACETIC ANHYDRIDE.

ACETO-BROMO-ACETIC ETHER *v.* BROMO-ACETO-ACETIC ETHER.

ACETO-BROMO-AMIDE *v.* ACETAMIDE.

ACETO-BUTYRIC ACID *v.* ACETYL-BUTYRIC ACID.

ACETO-CHLORO-AMIDE *v.* ACETAMIDE.

ACETO-CHLORHYDRIN *v.* GLYCERIN.

ACETO-CHLORHYDROSE: $C_{14}H_{19}ClO_9$ *i.e.* $C_6H_7Ac_4O_5Cl$. Formed by treating 1 mol. anhydrous glucose with 5 mol. AcCl, and purified by solution in chloroform, agitation with sodium carbonate, and evaporation.—Semifluid; sometimes crystalline. Dextro-gyrate. Bitter. Insol. in water, slightly sol. in CS_2, easily in alcohol, ether and chloroform. Distils in a vacuum, partly undecomposed. Gives up all its chlorine to alcoholic silver nitrate. Reduces Fehling's solution. Reconverted into glucose by heating with water (Colley, *C. R.*, 70, 401). H. W.

ACETO-CINNAMONE *v.* BENZYLIDENE-ACETONE.

ACETO-COUMARIC ACID *v.* COUMARIC ACID.

ACETO-CURCUMIN *v.* CURCUMIN.

ACETO-ETHYL NITRATE $C_2H_4O, 2C_2H_5NO_3$ (84°-86°) S.G. $\frac{12}{}$ 1·045. Formed by dry distillation of potassium ethyl-sulphate with potassium nitrate. Liquid, having a sweet taste and aromatic odour. Explodes violently when heated above its boiling point. Not miscible with water. Resolved by heating with potash-lye into aldehyde and nitric acid (Nadler, *A.* 116, 173). H. W.

ACETO-ETHYL-SUCCINIC ACID *v.* ACETYL-ETHYL-SUCCINIC ACID.

ACETO-ETHYL-THIENONE *v.* ETHYL-THIENYL METHYL KETONE.

ACETO-GLYCEROLS *v.* GLYCERIN.

ACETO-GUANAMINE *v.* GUANIDINE.

ACETO-TETRA-METHYLENE *v.* TETRAMETHYLENE METHYL KETONE.

ACETO-METHYL-THIENONE *v.* METHYL-THIENYL METHYL KETONE.

ACETONAMINES.

Di-Acetonamine

$C_6H_{13}NO$ *i.e.* $CH_3.CO.CH_2.CMe_2.NH_2$.

Preparation.—1. Dry ammonia-gas is passed into a flask containing boiling acetone, the conducting tube terminating just above the liquid; the resulting mixture of acetone-vapour and ammonia is passed through a tube heated to 100°, and then through a condensing tube; the distillate is neutralised with sulphuric acid diluted with an equal volume of water, and, after removing the ammonium sulphate which crystallises out, and distilling off unaltered acetone, the liquid is evaporated to dryness and the residue exhausted with boiling alcohol. Diacetonamine sulphate then crystallises out on cooling, and may be purified by recrystallisation from alcohol (Heintz, *A.* 174, 154).—2. Acetone saturated with ammonia is left to itself for three or four weeks, finely pounded oxalic acid is then added in quantity sufficient to form an acid salt, and a quantity of water equal to that of the acetone. The resulting crystalline precipitate is easily separated by boiling alcohol into insoluble ammonium oxalate and soluble diacetonamine oxalate. A further quantity of this last salt remains in the mother-liquor, together with salts of other bases (Sokoloff a. Latschinoff, *B.* 7, 1384).

Properties.—Free diacetonamine, separated from either of its salts by adding strong soda-lye and agitating with ether, is a colourless liquid lighter than water, having an ammoniacal odour and strong alkaline reaction; more soluble in cold than in hot water, mixes in all proportions with alcohol and ether; oxidises and turns brown on exposure to the air; forms crystalline salts with hydrochloric, sulphuric, and oxalic acids. By distillation it is for the most part resolved into NH_3 and mesityl oxide $C_6H_{10}O$, and on the other hand is easily formed by direct combination of these bodies: $C_6H_{10}O + NH_3 = C_6H_{13}NO$.

Salts.—$C_6H_{13}NOHCl$ crystallises from alcohol in rhombic prisms, v. sol. alcohol, resolved by dry distillation into NH_4Cl and $C_6H_{10}O$ (Heintz, *A.* 175, 252)—$(C_6H_{13}NO,HCl)_2PtCl_4,2H_2O$ crystallises from water, in which it is easily soluble (according to Sokoloff a. Latschinoff; also in dilute alcohol), in orange-yellow monoclinic prisms containing $2H_2O$, which they give off in a vacuum (H.); under ordinary pressure (S. and L.). The *normal oxalate* $(C_6H_{13}NO)_2C_2H_2O_4$ forms monoclinic tablets, very soluble in cold water, less soluble in alcohol than the acid salt. This latter $C_6H_{13}NO,C_2H_2O_4,H_2O$, forms monoclinic prisms; very soluble in hot, less in cold, water; easily in boiling alcohol, from which it separates out almost completely on cooling. The *picrate* $C_6H_{13}NO,C_6H_3(NO_2)_3O,H_2O$, forms gold-yellow needles, somewhat sparingly soluble in cold water. The *sulphate* $(C_6H_{13}NO)_2H_2SO_4$ forms monoclinic crystals (from alcohol).

Reactions.—1. HNO_2 decomposes the salts forming di-acetone alcohol and mesityl oxide:

$$2C_6H_{13}NO + 2HNO_2 =$$
$$C_6H_{12}O_2 + C_6H_{10}O + 2N_2 + 3H_2O.$$

2. *Chromic acid* mixture converts it into para-formaldehyde together with formic, acetic, and amido-iso-valeric acids $NH_2.CMe_2.CH_2.CO_2H$, and a small quantity of amido-iso-butyric acid $NH_2.CMe_2.CO_2H$ (Heintz, *A.* 198, 45).—3. Solid KOH forms an anhydride, $C_{12}H_{21}N_2O$ [83°]. This is v. sol. alcohol, chloroform, or benzene, m. sol. ether or light petroleum. Hot water decomposes it (Antrick, *A.* 227, 381). It forms a salt, $(C_{12}H_{21}N_2OHCl)_2PtCl_4$, when dry. Small prisms.—4. An aqueous solution of diaceto-

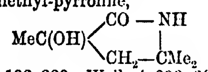
namine hydrochloride heated for ten hours at 120° with aqueous *hydrocyanic acid* forms the hydrochlorides of diacetonamine cyanhydrin and of nitrilo-diacetonamine, together with a little amido-iso-butyric acid (Heintz, *A.* 189, 231; 192, 340).—5. Diacetonamine oxalate boiled with alcoholic solutions of *aldehydes* forms condensation products.—6. *Sodium amalgam* reduces di-acetonamine to a secondary amido-iso-hexyl alcohol $CH_3.CH(OH).CH_2.CMe_2NH_2$.

CYANHYDRINS.

Di-Acetonamine cyanhydrin

$C_7H_{14}N_2O$ or $Me.C(OH)(CN).CH_2.CMe_2.NH_2$.

Carbylo-di-acetonamine.—Prepared as described above (*Reaction* 4).—Trimetric prisms. V. sol. water.. Decomposed by boiling alcohol into HCN and diacetonamine. Boiling HCl saponifies it, forming OXY-AMIDO-HEPTOIC ACID (*q. v.*), $Me.C(OH)(CO_2H).CH_2.CMe_2NH_2$, the greater part of which changes to its anhydride, di-oxy-tri-methyl-pyrroline,

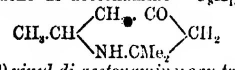


(Heintz, *A.* 192, 329; Weil, *A.* 232, 208 *v.* PYRROLINE).

Nitrilo-di-Acetonamine $C_7H_{14}N_2O$. The hydrochloride is obtained, as above stated, together with its isomeride. The free base is crystalline, easily soluble in water, sparingly in ether, and absorbs CO_2 from the air. Distinguished from carbylodiacetonamine by remaining unaltered when heated to 100°–110° with fuming hydrochloric acid. Resolved by boiling with baryta water into NH_3 and amido-trimethyl-oxybutyric acid $C_7H_{15}NO_3$ or its anhydride. The *platinochloride* $(C_7H_{14}N_2O,HCl)_2PtCl_4$ forms yellow rhombic prisms slightly soluble in water. The *oxalate* $C_7H_{14}N_2O,C_2H_2O_4$ forms small crystals m. sol. water, insol. alcohol (Heintz, *A.* 192, 342).

PRODUCTS FROM ALDEHYDES.

Ethylidene-di-acetonamine $C_8H_{15}NO$ or



[27°] (200°) *vinyl-di-acetonamine*; *oxy-tri-methyl-tetra-hydro-pyridine.*

Formation.—Together with tri-acetonamine by action of aldehyde and ammonia on acetone. In larger quantity as oxalate, by boiling the acid oxalate of diacetonamine (10 g.) for sixty hours in a reflux apparatus with aldehyde (10 g.) and alcohol (120 g.). The oxalate is washed with hot alcohol, and the free bases separated by potash (Heintz, *A.* 178, 326; 189, 214; 191, 122).

Preparation.—By boiling an alcoholic solution of di-acetonamine oxalate with paraldehyde (E. Fischer, *B.* 17, 1793).

Properties.—Solidifies at –15° to rectangular or six-sided plate ong prisms. Is deliquescent. Has a l g taste, smells like trimethylamine, but when warmed, like camphor.

Reduced by sodium amalgam to its dihydride or ethenyl-di-acetone-alcamine.

Salts.—$(B'HCl)_2PtCl_4$3aq. Flat prisms.—$B'_2H_2SO_4$. Minute needles, v. sol. water, sl. sol. alcohol.—$B'_2H_2C_2O_4$. Sl. sol. alcohol.—B'_4 $3H_2C_2O_4$.

A platino-chloride of vinyl-di-acetonamine and tri-acetonamine

$(C_8H_{15}NO.HCl + C_9H_{17}NO.HCl)PtCl_4 + 2H_2O$

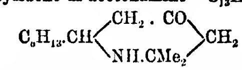
is formed by direct combination of its constituents. 100 pts. water at 14° dissolve 8·65 pts. of the anhydrous salt (Heintz, *J.* 1877, 442).

Pentylidene-di-acetonamine $C_{11}H_{21}NO$ or

Valeral-di-acetonamine; *oxy-di-methyl-iso-butyl-tetra-hydro-pyridine* [15°–22°]. From valeric aldehyde and alcoholic di-acetonamine oxalate (Antrick, *A.* 227, 367). Needles in stars (from ether). Insol. water, sol. alcohol, ether, benzene, and petroleum.

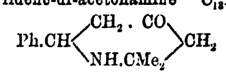
Salts.—$B'_2H_2C_2O_4$. Needles [190°]. V. sl. sol. cold water or alcohol.—$(B'HCl)_2PtCl_4$ [205°].

Heptylidene-di-acetonamine $C_{13}H_{25}NO$ or



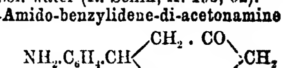
Oxy-di-methyl-hexyl-tetra-hydro-pyridine [29·5°]. From œnanth-aldehyde and alcoholic di-acetonamine oxalate (Antrick, *A.* 227, 370). Needles (from ether). *Oxalate* $B'_2H_2C_2O_4$ [c. 150°].

Benzylidene-di-acetonamine $C_{13}H_{17}NO$ or



Oxy-phenyl-di-methyl-tetra-hydro-pyridine [61°] (230°). Obtained as oxalate, by boiling 1 pt. benzaldehyde, 1 pt. acid diacetonamine oxalate, and 12 pts. alcohol, gradually separating as a powder which may be purified by crystallisation from water. Colourless needles or monoclinic prisms (from ether). V. sol. alcohol and ether; sl. sol. water. Tasteless, has a faint aromatic odour. Forms normal and acid salts.—$C_{13}H_{17}NOHCl$. Crusts or druses of crystals.—$(C_{13}H_{17}NO.HCl)_2PtCl_4$. Warty groups of crystals, or when separated from alcohol on addition of ether, elongated six-sided tablets. Slightly soluble in hot, insol. in cold alcohol. The *aurochloride* forms pale-yellow crystals.—$C_{13}H_{17}NOHNO_3 + 2H_2O$ (?). Small crystals, moderately soluble in cold water.—$(C_{13}H_{17}NO)_2H_2SO_4$. Small crystals, easily soluble in water, very slightly in absolute alcohol.—$(C_{13}H_{17}NO)_2,C_2H_2O_4$. Microscopic crystals, nearly insoluble in alcohol, v. sl. sol. water (R. Schiff, *A.* 193, 62).

***m*-Amido-benzylidene-di-acetonamine**



From the nitro-derivative by reduction with $SnCl_2$. Oil. *Salts.*—$B''H_2C_2O_4$ [113°].

***p*-Amido-benzylidene-di-acetonamine.**—From the nitro-derivative by $SnCl_2$. *Salt.*—$B''H_2C_2O_4$.

***o*-Nitro-benzylidene-di-acetonamine**

From *o*-nitrobenzoic aldehyde and alcoholic di-acetonamine oxalate.

Salts.—$B'_2H_2C_2O_4$.—B'HCl.—$(B'HCl)_2PtCl_4$.

***m*-Nitro-benzylidene-di-acetonamine.**

Salts.—B'HCl [208°].—$(B'HCl)_2PtCl_4$ [203°].

***p*-Nitro-benzylidene-di-acetonamine** [142·5°]. Needles (from ether). Nearly insol. light petroleum.

Salts.—B'HCl aq. [c. 206°].—$(B'HCl)_2PtCl_4$.

p-Oxy-benzylidene-di-acetonamine

$$HO.C_6H_4.CH\left\langle\begin{matrix}CH_2 . CO\\ NH.CMe_2\end{matrix}\right\rangle CH_2.$$

From di-acetonamine oxalate (5 pts.), *p*-oxy-benzoic aldehyde (4 pts.), and alcohol (20 pts.)

Acid oxalate $B'H_2C_2O_4$.

Methyl derivative

$$MeO.C_6H_4.CH\left\langle\begin{matrix}CH_2 . CO\\ NH.CMe_2\end{matrix}\right\rangle CH_2.$$

From anisaldehyde and di-acetonamine oxalate.

Oxalate $B'_2H_2C_2O_4$ [210°].

Cinnamylidene-di-acetonamine

$$Ph.CH{:}CH.CH\left\langle\begin{matrix}CH_2 . CO\\ NH.CMe_2\end{matrix}\right\rangle CH_2\ \tfrac{1}{2}\ aq.\ [49^\circ].$$

From cinnamic aldehyde, diacetonamine, and boiling alcohol. Yellow needles (from alcohol). Easily soluble in ether, light petroleum, chloroform and benzene, sparingly in water.

Vanillo-di-acetonamine $C_{14}H_{19}NO_3$ *i.e.*

$$C_6H_3(OMe)(OH)CH\left\langle\begin{matrix}CH_2 . CO\\ NH.CMe_2\end{matrix}\right\rangle CH_2$$

is obtained by boiling equal parts of vanillin and acid diacetonamine oxalate -diacetonamine cohol, whereby normal This salt forms either oxalate is three or yellowish crystalline crusts; a white water, insol. alcohol and ether. The base is an alkaline oil, slightly soluble in water.—$C_{14}H_{19}NO_3HCl$ is easily soluble in alcohol, and precipitated therefrom by ether.—$(C_{14}H_{19}NO_3HCl)_2PtCl_4$.—$C_{14}H_{19}NO_3HNO_3$. Very small crystals, m. sol. water, and cold alcohol, $(C_{14}H_{19}NO_3)_2H_2SO_4$: laminæ. $(C_{14}H_{19}NO_3)_2C_2H_2O_4$: crystalline, v. sl. sol. water, insol. alcohol (Heintz, *A.* 194, 53).

ALKYL-DI-ACETONAMINES.

Methyl di-acetonamine

$C_7H_{15}NO$ *i.e.* $COMe.CH_2.CMe_2.NHMe$, is formed, together with other bases, when acetone saturated with methylamine is left to itself for several weeks. The base is ppd. as acid oxalate, and purified by conversion into platinochloride.—Free methyldiacetonamine is very unstable, quickly splitting up into methylamine and mesityl oxide. The *hydrochloride* is deliquescent. The *platinochloride* $(C_7H_{15}NOHCl)_2PtCl_4$ crystallises in large light-red rhombic prisms, easily soluble in water, nearly insoluble in alcohol. The *platinosochloride* $(C_7H_{15}NOHCl)_2PtCl_2$, produced simultaneously with the platinochloride, forms dark red crystals. The *aurochloride* $C_7H_{15}NO,HCl,AuCl_3$, forms short prisms, m. sol. cold, v. sol. hot, water, alcohol, and ether. The *normal oxalate* $(C_7H_{15}NO)_2C_2H_2O_4$ forms indistinct very deliquescent crystals, very soluble in absolute alcohol; the *acid oxalate* $C_7H_{15}NOC_2H_2O_4$ crystallises in small prisms, m. sol. absolute alcohol. The *picrate* forms yellow needles (Götschmann, *A.* 197, 38).

Dimethyldiacetonamine

$C_8H_{17}NO$ *i.e.* $COMe.CH_2.CMe_2.NMe_2$, is formed on heating a solution of dimethylamine in acetone at 100°-105° in a scaled tube. Free dimethyldiacetonamine has not been obtained as it very easily splits up into dimethylamine and mesityl oxide. The *platino-chloride* $(C_8H_{17}NOHCl)_2PtCl_4$ crystallises in small tablets; the *auro-chloride* in golden needles, sl. sol. water; the *nitrate* and *sulphate* in long colourless deliquescent needles v. sol. alcohol. The *acid oxalate*, $C_8H_{17}NOC_2H_2O_4$, is crystalline, v. sol. water and alcohol, nearly insoluble in ether (Götschmann, *A.* 197, 27).

Ethyldiacetonamine

$C_8H_{17}NO$ *i.e.* $MeCO.CH_2.CMe_2.NHEt$, is obtained by heating a solution of ethylamine in acetone at 80° for six hours. $C_{16}H_{36}N_2O_2PtCl_6$, light red hexagonal plates, insol. ether and alcohol, soluble in alcohol containing HCl. S. 1·16 at 16°. *Platinosochloride*: $C_{16}H_{36}N_2O_2PtCl_4$; dark red prisms. S. 6·62 at 21°, insoluble in ether and in alcohol.—$C_8H_{17}NOHCl$ forms hygroscopic microcrystals decomposing at 150°.—$C_8H_{18}NOAuCl_4$ crystallises in large lemon-yellow rhombic plates. S. 2·48 at 22°; easily soluble in alcohol and ether; melts under water at about 70°.—The *nitrate* forms small needles.—$(C_8H_{17}NO)_2H_2SO_4$ forms tufts of needles.—$(C_8H_{17}NO)_2C_2H_2O_4$, concentric groups of hygroscopic needles.—$C_8H_{17}NOC_2H_2O_4$; needles.—The *picrate* $C_8H_{17}NO,C_6H_2(NO_2)_3OH$ forms short needle-shaped prisms v. sol. water, insol. alcohol Free ethyldiacetonamine splits up even in the cold into ethylamine and mesityl oxide (Eppinger, *A.* 204, 50). The prolonged heating of ethylamine with acetone gives rise only to ethyl-diacetonamine, not to any base analogous to triacetonamine. Diethylamine does not appear to form any compound with acetone (Eppinger).

Dehydrodiacetonamine $C_6H_{11}N(?)$ contained in the mother-liquors of the preparation of acid diacetonamine oxalate, and passes over on distilling them with an alkali. The platinochloride forms slightly sol. laminæ (Heintz, *A.* 183, 276).

Triacetonamine $C_9H_{17}NO$ *i.e.*

$$NH\left\langle\begin{matrix}CMe_2.CH_2\\ CMe_2.CH_2\end{matrix}\right\rangle CO$$

Oxy-tetra-methyl-tetra-hydro-pyridine [58°] (hydrated); [39·6°] (dry). *Formation.*—1. Together with diacetonamine, by the action of ammonia on acetone, especially at high temperatures (Heintz, *A.* 174, 133).—2. By prolonged boiling of acetone with a solution of diacetonamine : $C_6H_{13}NO + C_3H_6O = C_9H_{17}NO + H_2O$ (Heintz, *A.* 178, 305). This, according to Heintz, is the best mode of preparing triacetonamine. It is purified by crystallisation of the oxalate. Triacetonamine separates from a solution of the normal oxalate mixed with KOH, as a hydrate $C_9H_{17}NO,H_2O$, which crystallises from anhydrous ether in large square tablets, and the mother-liquor on further evaporation and cooling to a very low temperature yields long needle-shaped crystals of anhydrous triacetonamine. Hydrated crystals rhombic $a : b : c = 0·9886 : 0·9768 : 1$. Triacetonamine sublimes slowly, even at ord. temp. Distils without alteration. Decomposed at 150°-200° by H_2SO_4 or P_2O_5, but does not yield definite products. Heated at 100° for 16 hours with fuming hydrochloric acid it yields diacetonamine, dehydropentacetonamine and other products. With chromic acid mixture it gives isopropyl-butyl-amine di-carboxylic acid: $C_9H_{17}NO_4$ *i.e.* $CO_2H.CMe_2.NH.CMe_2.CH_2.CO_2H$ (Heintz, *A.* 198, 69). With ethyl iodide it yields NH_2Et, $NHEt_2$, NEt_3, NEt_4I, dehydrotriacetona-

mine, and other products, but no ethylated triacetonamines (Heintz, *A.* 201, 100).

Salts.—B′HCl is easily soluble in alcohol, and separates therefrom on addition of ether, in prisms.—$(B'HCl)_2PtCl_43H_2O$ crystallises from hot water in long, dark, gold-coloured needles, v. sl. sol. alcohol, insol. ether. By exposing the alcoholic solution to sunlight, or heating the aqueous solution for several hours, it is reduced to $(B'HCl)_2PtCl_22H_2O$, which is much less soluble in water than the platino-chloride, and crystallises in dark red needles or rhombic prisms.—$(C_9H_{17}NO)_2H_2SO_4$: delicate needles or prisms v. sol. in water, insol. alcohol and ether.—$C_9H_{17}NO,HNO_3$: rhombic crystals—$a:b:c$ = 1·2738 : 1 : 1·0251.—$(C_9H_{17}NO)_2H_2CrO_4$. Small light yellow crystals converted into the acid salt by recrystallisation from hot water.—$(C_9H_{17}NO)_2H_2Cr_2O_7$. Orange-red prisms (Heintz, *A.* 198, 87).—$(C_9H_{17}NO)_2C_2H_2O_4$ forms long needles, v. sol. water, v. sl. sol. alcohol.—$C_9H_{17}NO,C_2H_2O_4$. Triclinic crystals, v. sol. water; resolved by boiling with alcohol or ether into the normal salt and oxalic acid (Heintz, *A.* 178, 326).

Triacetonamine Nitrosamine $C_9H_{16}(NO)NO$ [73°], S.G. 1·14, is formed by heating aqueous triacetonamine hydrochloride with KNO_2 at 85°. Long needles (from alcohol). V. sol. alcohol and ether. Resolved by KOH into nitrogen, water, and phorone, also by prolonged boiling in aqueous solution. By heating with HCl or H_2SO_4, it is for the most part reconverted into triacetonamine (Heintz, *A.* 185, 1; 187, 233).

Tri-acetone-diamine

$C_9H_{20}N_2O$ *i.e.* $(NH_2.CMe_2.CH_2)_2CO$.

Found in small quantity amongst the products of the action of ammonia on acetone; produced more abundantly when a mixture of 1 pt. acetone, 2 pts. NH_3Aq, and 1 pt. CS_2, is left at rest for a month; $3C_3H_6O + 2NH_3 = C_9H_{20}N_2O + 2H_2O$. Oily liquid soluble in water, somewhat sparingly in ether. B″2HCl forms prismatic crystals, decomposing at 200°.—$B''2HCl,PtCl_4$ is slightly soluble in cold, easily in hot water, insoluble in ether.—$B''C_2H_2O_4$; flat needles, nearly insoluble in alcohol, much more soluble in water, than the acid salt.—$B''2H_2C_2O_4$ aq; monoclinic prisms (Heintz, *A.* 203, 336).

Dehydro-tri-acetonamine $C_9H_{15}N$ (*Tetra-methyl-di-hydro-pyridine?*) (158°) (H.); (163°) (C. S.).

Occurs as oxalate, together with tri-acetonamine, in the mother liquor got in preparing di-acetonamine oxalate (*q. v.*), and may be separated therefrom by distillation with potash (Heintz, *A.* 174, 166; 183, 276).

Preparation.—Acetone (20g.), acetamide (8g.), and $ZnCl_2$ (30g.), are heated for 6 hours at 140° (Canzeroni a. Spica, *G.* 14, 341). Another base (240°) is a by-product in this reaction. It appears to be $C_{15}H_{27}N$. Its platino-chloride forms dodecahedra.

Properties.—Oily liquid which readily oxidises, becoming brown.

Salts.—$(B'HCl)_2PtCl_4$. Rhombohedra (from water). V. sl. sol. cold water, insol. alcohol.—$B'HAuCl_4$ [127°]. Long yellow prisms (from dilute alcohol). Insol. water.

Dehydro-penta-acetonamine

$C_{15}H_{25}N = 5C_3H_6O + NH_3 - 5H_2O$.

Is formed together with ammonia and di-acetonamine by heating tri-acetonamine with fuming HCl at 130°, the hydrochloride then separating as a crystalline powder, sparingly soluble in water. The base separated therefrom by potash is an oily liquid (Heintz, *A.* 181, 70). H. W.

ACETO-NAPHTHYL-THIAMIDE *v.* α-NAPHTHYLAMINE.

ACETONE C_3H_6O *i.e.* $CH_3.CO.CH_3$.

Di-methyl Ketone.

M. w. 58 (55·6°-55·9° cor.) (Perkin, *C. J.* 45, 478); (56°) (Dumas; R. Schiff); (56·3°) at 760 mm. (Kopp, Regnault, Zander); (56·53° cor.) (Thorpe, *C. J.* 37, 212). S.G. $\frac{0}{}$ ·814; $\frac{13·9}{}$ ·799 (Kopp, *A.* 64, 214); $\frac{0}{4}$ ·8186 (T.); $\frac{15}{15}$ ·7965; $\frac{25}{25}$ ·7867 (P.); $\frac{0}{0}$ ·8125 (Z.); $\frac{20}{4}$ ·7920 (Brühl); $\frac{56}{4}$ ·7506 (R. Schiff, *A.* 220, 103). V.D. 2·00 (Dumas). C.E. (0°-10°) ·00138 (T.). S.V. 77·08 (S.); 77·3 (Z.); 76·78 (T.). H. F. p. 65,000 (Berthelot); 58,710 (Thomsen). H. F. v. 57,260 (Th.). μ_β 1·3639. R_∞ 25·55 (Brühl). M. M. 3·514 at 15·2° (P.).—Occurs in the urine, blood, and brain of diabetics (Markownikoff, *B.* 8, 1683; Peters, Kaulich, Betz, *J.* 1861, 805).

Formation.—1. By the dry distillation of acetates: *e.g.* $(MeCO.O)_2Ba = Me_2CO + BaCO_3$.—2. From zinc-methyl and acetyl chloride;

(*a*) $MeCOCl + ZnMe_2 = MeCClMe.OZnMe$,

(*b*) $MeCClMe.OZnMe + H_2O = Me_2.CO + HCl + ZnO + CH_4$

(Freund, *A.* 118, 1).—3. By treating bromo- or chloro-propylene with aqueous hypochlorous acid and mercuric oxide, whereby chloracetone is formed:

$$2C_3H_5Cl + 2HOCl + HgO = HgCl_2 + H_2O + 2(CH_2Cl.CO.CH_3),$$

and reducing this compound to acetone with zinc and HCl (Linnemann, *Bl.* [2] 6, 216).—4. By treating the isomeric compound, propylene oxide, with sodium-amalgam, and dehydrogenising the resulting isopropyl alcohol with chromic mixture, $C_3H_6O + H_2 = (CH_3)_2CH.OH$, and

$$(CH_3)_2CH.OH + O = H_2O + (CH_3)_2CO$$

(Linnemann, *A.* 140, 178). Berthelot (*C. R.* 68, 334), effects the oxidation with aqueous chromic acid.—5. By the action of an aqueous solution of mercuric bromide (Kutscheroff, *B.* 14, 1541), or chloride (*B.* 17, 15), on allylene.—6. By passing aldehyde vapour over red-hot lime (Schloemilch, *Z.* 5, 336).—7. Together with propionic aldehyde, by heating a dilute aqueous solution of propylene glycol at 180°-190° (Eltekoff, *J.* 11, 409).—8. By heating propylene bromide with water at 170°-180°:

$$C_3H_6Br_2 + H_2O = 2HBr + C_3H_6O$$

(Linnemann, *A.* 161, 58).—9. By heating α-α-di-chloro-propane CMe_2Cl_2 with silver acetate and alcohol in sealed tubes at 100°:

$CMe_2Cl_2 + 2AgCO_2Me = 2AgCl + 2COMe_2 + CO_2$.—10. Together with a bromine compound (probably $CHMe_2Br$) by the action of zinc and dilute sulphuric acid on the product $C_3H_4Cl_2Br_2O$, formed by the action of bromine on dichlorhydrin (Lange, *B.* 6, 98).—11. By distilling with water the product formed, with evolution of HCl, on dissolving chloro-propylene Me.CCl:CH$_2$ in sulphuric acid (Oppenheim, *A.* Suppl. 6, 365).—12. Together with mesitylene, on distilling with water a solution of allylene in sulphuric acid (Schrohe, *B.* 8, 367).—13. Together with other

products, by the action of lime on glycerin (Tawilderow, *B.* 12, 1487).—14. Together with isobutyric aldehyde, by oxidation of iso-butyl alcohol.—15. By oxidising with chromic acid the hexylene obtained by the action of alcoholic potash on di-methyl-isopropyl-carbinyl iodide (Pawlow, *Bl.* [2] 29, 375).—16. By the action of nascent zinc-methyl on acetic oxide (Saytzeff, *Z.* [2] 7, 104): $(COMe)_2O + ZnMe_2 = ZnO + 2COMe_2$.—17. Together with other products, by the action of zinc-sodium on a mixture of methyl iodide and acetic oxide (S.).—18. By the dry distillation of wood: occurs therefore in crude wood-spirit; also of sugar, gum, or starch, with 8 pts. lime (Fremy, *A. Ch.* 59, 7).—19. By dry distillation of citric acid, and in the oxidation of that acid by potassium permanganate, or by MnO_2 and dilute sulphuric acid (Péan de St. Gilles, *A. Ch.* [3] 55, 374).

Preparation.—1. By dry distillation of barium or calcium acetate. The barium salt decomposes at a moderate heat, and when dry and pure yields pure colourless acetone. The calcium salt requires a higher temperature and yields a distillate contaminated with an empyreumatic oil (dumasin) and other products.—2. By distilling in an iron retort or quicksilver bottle, a mixture of lead acetate (2 pts.) and quick lime (1 pt.), rectifying over calcium chloride, and finally distilling over the water-bath. The product may be purified from wood-spirit by distillation over calcium chloride, or better by combining the acetone with sodium hydrogen sulphite, and decomposing the resulting compound by an acid or alkali; also by converting the methyl alcohol into an ether (oxalic or benzoic). Crude acetone may also be purified by treating it with potassium permanganate, which does not attack pure acetone at ordinary temperatures.

Properties. — Limpid, very mobile liquid having a spirituous and slightly empyreumatic odour and biting taste. Very inflammable; burns with a white smokeless flame, mixes in all proportions with water, alcohol, and ether. Dissolves camphor, fats, and resins. Separated from aqueous solution by $CaCl_2$ and by KOH (difference from alcohol). Even if boiling between 56° and 58° it is liable to contain methylacetal, $CH_3.CH(OCH_3)_2$; this can be detected by heating with conc. HCl, for it then gives off MeCl. Acetone reacts with hydroxylamine and with phenyl-hydrazine (*v.* ACETOXIM, ACETONE TOLYL-HYDRAZIDE). It does not restore the ducea of a solution of a rosaniline salt that forms dat-eached by SO_2 (Schiff).

$C_7H_{13}NO,HCl$.—1. An alcoholic liquid supposed cold, v. sol. hot, is mixed with an equal volume *normal oxalate* (C_7... of benzoic aldehyde and tinct very deliquescent ...H are added. After some absolute alcohol; the *acid* di-benzylidene-acetone crystallises in small pris... olve in H_2SO_4 giving alcohol. The *picrate* form. Ponder, *A.* 223, (Götschmann, *A.* 197, 38). ueous KOH and

Dimethyldiacetonamine 3. A solution

$C_8H_{17}NO$ *i.e.* $CO.Me.CH_2.CMe_2$. previously is formed on heating a solution of A black mine in acetone at 100°–105° in a sc...rs, but Free dimethyldiacetonamine has not bes this tained as it very easily splits up into dim...ve to amine and mesityl oxide. The *platino-chlo*... be $(C_8H_{17}NOHCl)_2PtCl_4$ crystallises in small table

Reactions.—1. Acetone-vapour passed through a *red-hot tube* deposits carbon and yields so-called dumasin, also naphthalene, CO_2, CH_4, and H (Barbieri a. Roux, *C.R.* 102, 1559).—2. By *nascent hydrogen* (sodium-amalgam and water) acetone is converted into isopropyl alcohol: $Me.CO.Me + H_2 = Me.CHOH.Me$ (Friedel, *C.R.* 55, 53).—3. *Chlorine-gas* passed into acetone displaces 1 or 2 ats. H, forming C_3H_5ClO and $C_3H_4Cl_2O$, but does not remove the whole of the hydrogen, even in sunshine. Grabowski (*B.* 8, 1438), by passing chlorine into pure acetone, assisting the action by heat towards the end, obtained in addition to dichloracetone, two bodies $C_5H_7Cl_3O$ and $C_6H_7Cl_3O$. The former is a liquid insoluble in water (186°). S.G. 1·330 at 29°. V.D. 6·60 (calc. 6·56). Decomposed by strong potash-lye, with separation of chloroform. The second body, $C_6H_7Cl_3O$, is also liquid (206°–208°). S.G. 1·326 at 26°. V.D. 7·55 (calc. 7·0). Completely decomposed by strong potash-lye or sulphuric acid. Perhaps trichlorotrimesityloxide. When acetone is treated with excess of chlorine, and the product first with KOH and then with HCl, isapoglucic acid $C_9H_{10}O_5$ is produced. With alcoholic potash, on the other hand, a body $C_6H_{10}O_5$ (?) is formed, together with an acid whose lead-salt has the composition $Pb(C_7H_9O_3)_2$ (Mulder, *J.* 1868, 494).—4. *Chlorine*, in presence of alkalis, converts acetone into chloroform:

$$C_3H_6O + 6Cl_2 + H_2O = 2CHCl_3 + CO_2 + 6HCl.$$

Bromine acts in like manner, producing bromoform, and iodine forms iodoform.—5. When acetone saturated with HCl-gas is mixed, after 8–14 days, with *water*, a heavy brownish oil separates, consisting mainly of compounds of HCl with mesityl oxide, $C_6H_{10}O$ ($= 2C_3H_6O - H_2O$) and phorone, $C_9H_{14}O$ ($= 3C_3H_6O - 2H_2O$). The mesityl compound $C_6H_{12}OCl_2$, heated with KCN and then with KOH, yields the K-salt of a monobasic acid $C_8H_{13}NO_3$ (*v.* MESITONIC ACID), thus: $C_6H_{12}OCl_2 + 2KCN = 2KCl + C_6H_{12}O(CN)_2$; and $C_6H_{12}O(CN)_2 + KOH + H_2O = NH_3 + KC_8H_{12}NO_3$. The phorone compound, similarly treated, yields a neutral azotised body crystallising in shining plates and subliming at about 300° (Maxwell Simpson, *Pr.* 16, 364). According to Pinner (*B.* 14, 1070) the neutral body is a nitrile $C_{11}H_{18}O_2N_2$, formed according to the equation $3C_3H_6O + 2HCN = H_2O + C_{11}H_{18}O_2N_2$; it crystallises in plates melting above 320°. Heated with aqueous hydrochloric acid it gives phoronic acid $C_{11}H_{18}O_2$ [*q. v.*]: $C_9H_{18}O_2(CN)_2 + 4H_2O = 2NH_3 + H_2O + C_9H_{16}O(CO_2H)_2$.—6. By distillation with strong *sulphuric acid*, acetone yields mesitylene, $C_9H_{12} = 3C_3H_6O - 3H_2O$; but when mixed with H_2SO_4 in a cooled vessel it forms mesityl-sulphonic acid $C_3H_5.SO_3H$, which, when heated with potash, yields mesityl oxide (Hlasiwetz, *J.* 1856, 487).—7. With PCl_5 acetone yields chloropropylene C_3H_5Cl and di-chloro-propane $C_3H_6Cl_2$ (Friedel, *A.* 112, 236).—8. With *bromine* acetone unites directly, forming $C_3H_6OBr_2$, a viscid, very unstable liquid, heavier than water (Linnemann, *A.* 125, 307). According to E. J. Mulder, however (*J. pr.* 91, 47), it gives rise to substitution-products.—9. With HI acetone yields iodopropylene, C_3H_5I; with PI_3 a solid and two liquid iodides (Harnitz-Harnitzky, *Z.* 1863, 416). According to Berthelot (*Bl.* [2] 7, 69), acetone treated with HI yields propane.—

10. With *iodine chloride* acetone yields $C_3H_4I_2O$ (Maxwell Simpson, *Laboratory*, p. 79).—11. *Electrolysis* of a mixture of acetone and dilute sulphuric acid produces acetic, formic, and carbonic acids (Friedel, *J.* 1859, 338).—12. By *chromic acid* mixture it is oxidised to acetic and carbonic acids.—13. Acetone heated with *ammonia* yields a mixture of three bases, the composition and mode of formation of which are indicated by the following formulæ:—

Diacetonamine	$C_6H_{13}NO = 2C_3H_6O + NH_3 - H_2O$
Triacetonamine	$C_9H_{17}NO = 3C_3H_6O + NH_3 - 2H_2O$
Dehydrotriacetonamine .	$C_9H_{15}N = C_9H_{17}NO - H_2O$.

With *methylamine*, in like manner, acetone yields methyldiacetonamine $C_7H_{15}NO$ and other bases. With *dimethylamine* only dimethyldiacetonamine $C_8H_{17}NO$.—14. With *hydroxylamine*, acetone forms ACETOXIM [*q.v.*] $Me_2C:NOH$, which crystallises in prisms [60°], (135°).—15. *Sodium* strongly attacks acetone, with formation of crystallised pinacone hydrate $C_6H_{12}O\ 7H_2O$ and liquid phorone $C_9H_{14}O$ thus: $2C_3H_6O + Na_2 = Na_2O + C_6H_{12}O$, and $3C_3H_6O - 2H_2O = C_9H_{14}O$ (Städeler, *A.* 111, 277).—16. Heated with *aniline hydrochloride* at 180° it forms di-methyl-quinoline (Engler a. Riehm. *B.* 18, 2245, 3296).—17. *Caustic alkalis, e.g.* KOH and CaO, exert a dehydrating action on acetone and form condensation-products varying in composition, according to the proportion of water abstracted, viz.:

		B. P.
Xylite-naphtha	$C_{12}H_{22}O_3 = 4C_3H_6O - H_2O$ ..	110°–120°
Mesityl oxide	$C_6H_{10}O = 2C_3H_6O - H_2O$	131°
Mesitylene ..	$C_9H_{12} = 3C_3H_6O - 3H_2O$..	155°–160°
Phorone	$C_9H_{14}O = 3C_3H_6O - 2H_2O$..	216°–220°
Xylite-oil ..	$C_{12}H_{18}O = 4C_3H_6O - 3H_2O$ above	250°

Vapour of acetone passed over strongly heated KOH or potash-lime is resolved into methane and carbonic acid, $C_3H_6O + 2KOH = K_2CO_3 + 2CH_4$. At a lower temperature the chief products are acetic acid, formic acid, and hydrogen, $C_3H_6O + 2KOH + H_2O = KC_2H_3O_2 + KCHO_2 + 3H_2$ (Dumas a. Stas, *A. Ch.* [2] 73, 149; Persoz, *Rev. Scient.* 1, 51).—18. Acetone heated with $ZnCl_2$ yields hexa-methyl-benzene C_6Me_6 (W. H. Greene, *C. R.* 87, 931).—19. Gently heated with $AlCl_3$, it yields mesityl oxide, phorone, and other products (Louise, *C. R.* 95, 602).—20. Dry $PtCl_4$ dissolves in acetone, and the solution when evaporated leaves a brown resinous mass containing a yellow crystalline substance, $C_6H_{10}OPtCl_2$ (?), called *Acechloride of Platinum*, or *Chloroplatinite of Mesityl* (Zeise, *A.* 33, 29).—21. On adding HCl to a mixture of acetone, with potassium cyanide and sulphocyanide, the compound $C_5H_7O_2NS$ is obtained. This compound heated with HCl is resolved into CO_2, NH_3, and α-oxy-iso-butyric acid. With silver nitrate it yields $C_5H_6AgO_2NS$ (Urech, *B.* 6, 1113).—22. By action of alkalis or of HCl-gas on a mixture of 1 mol. acetone and 2 mol. benzaldehyde, DIBENZYLIDENE-ACETONE (*q. v.*) PhCH:CH.CO.CH:CHPh is obtained (Claison a. Claparede, *B.* 14, 349). By the action of alkalis on a solution of *o*-nitro-benzaldehyde in acetone, methyl *o*-nitro-β-oxy-β-phenyl-ethyl ketone [68°] is formed according to the equation

$$NO_2.C_6H_4.CHO + CO(CH_3)_2 =$$
$$NO_2.C_6H_4.CH(OH).CH_2.COCH_3$$

(Baeyer a. Drewsen, *B.* 15, 2856).—The corresponding *para*-compound [58°] is obtained in like manner from acetone and *p*-nitro-benzaldehyde (Baeyer a. Becker, *B.* 16, 1968).—23. With *furfuraldehyde*, acetone forms a compound crystallising in long white needles [37°] (J. G. Schmidt, *B.* 14, 574)—*v.* FURFURYLIDENE-ACETONE. 24. With *pyrrol* in presence of HCl it forms $C_{14}H_{16}N_2$, [291°] (Baeyer, *B.* 19, 2184).

Combinations.—1. With **Bisulphites.** Formed by direct combination. $C_3H_6(OH)SO_3NH_4$ crystallises in laminæ (Städeler, *A.* 111, 307)—$C_3H_6(OH)SO_3Na$.—Laminæ, moderately soluble in water, less in alcohol. Gives off acetone when boiled with aqueous sodium carbonate (Limpricht, *A.* 93, 238)—$C_3H_6(OH)SO_3K$ (L.). 2. With **Mercuric Oxide** $2C_3H_6O\ 3HgO$. Formed by mixing acetone with mercuric chloride and weak potash-lye, dialysing the filtered liquid, and precipitating the liquid remaining in the dialyser with acetic acid.—Gelatinous precipitate which becomes resinous on drying. Its solution gelatinises when heated or when merely left at rest (Emerson Reynolds, *Pr.* 19, 431). Formed also by dissolving HgO in acetone (Kutscheroff, *B.* 17, 20).

Acetone-boric Acid, $C_3H_6O(BHO)_2$ [60°]. Formed together with (*a*) and (β) acetone-fluoboric acid, and hydrocarbons, on saturating acetone with boron fluoride and distilling the product. (*a*) *Acetonefluoboric acid*, $C_3H_6O\ 3HFB_2O_4$ (120°–123°); the isomeric (β) modification [36°] (90°–92°) forms shining white laminæ. All three compounds fume in the air, burn with green flame, and are quickly decomposed by water, yielding boric acid and acetone hydrofluoric acid (Landolf, *C. R.* 89, 173).

Acetone-hydrofluoric Acid C_3H_6OHF (55°) obtained by fractional distillation from the product of the action of water on acetone-fluoboric acid. An inflammable liquid with pleasant ethereal odour (Landolf, *C. R.* 96, 580). Another compound, $C_3H_6O\ 2HF$ (–12°) is gaseous at ordinary temperatures.

Acetone-sulphonic Acid $CH_3.CO.CH_2.SO_3H$. Formed as K-salt by treating dichloracetone (118°) with a strong solution of potassium sulphite: $C_3H_4Cl_2O + K_2SO_3 + H_2O =$

$$K_2SO_4 + HCl + C_3H_5ClO, \text{ and}$$
$$C_3H_5ClO + K_2SO_3 = KCl + C_3H_5O.SO_3K.$$

The K-salt may be extracted from the product by boiling alcohol, and separates therefrom in white laminæ. Very soluble in water, not decomposed by boiling with dilute acids. Boiled with strong potash-lye, it yields sulphite and perhaps an acetone-alcohol (Bender, *Z.* 1870, 162; *B.* 4, 517). *Salts.*—KA' Plates (from alcohol V. e. sol. water—BaA'_2 aq. Plates.—PbA'_2 aq. [140°]—$CuA'_2\ 1\frac{1}{2}$aq. Greenish plates.

Acetone-phosphorous Acid $C_3H_6O.PO_2H_2$. Remains on distilling acetone with I and P. $(C_3H_6O.PO_2)_2Ba$ is amorphous, soluble in water, insoluble in alcohol (Mulder, *J.*, 1864, 329).

Acetone-cyanhydrin $CH_3.C(CN)(OH).CH_3$ (*Oxyisobutyronitrile*). Formed by the action of aqueous HCN (20 p.c.) on acetone, or by the action of nascent HCN on acetone diluted with ether.

It is very unstable, for even on evaporation of its solution it changes into di-acetone-cyanhydrin with evolution of HCN (Tiemann a. Friedländer, *B.* 14, 1970). Alcoholic NH_3 at 60° converts it into α-amido-iso-butyronitrile $CH_3.C(CN)(NH_2).CH_3$ whence HCl forms α-amido-

iso-butyric acid. Alcoholic HCl forms the imido-ether $Me_2C(OH)C(OEt):NH$ (Pinner, *B.* 17, 2009).

Diacetone cyanhydrin $CMe_2(CN).O.CMe_2(OH)$, is prepared by adding 1 mol. HCl (gaseous or aqueous) to 1 mol. KCN immersed in acetone, dissolving the product in ether, and evaporating (Urech, *A.* 164, 259). Thick shining anhydrous prisms, easily soluble in water, alcohol, and ether. Melts at 135°–152° and sublimes below its melting point in long needles. Decomposed at ord. temp. by HCl into [illegible] acetone, and α-oxy-iso-butyric acid.

Substitution Products v. CHLORO-ACETONE, CHLORO-BROMO-A[illegible] ACETONE, CYANO-ACETONE, THIO-ACETO[illegible].

Meta-acetone. — This name was [illegible] Fremy (*A. Ch.* [2] 59, 6) to an oil o[illegible] among the products of the distillation of [illegible] starch, or gum, with quicklime. He ascribe[illegible] it the formula $C_6H_{10}O$ and boiling-point 84°. Gottlieb (*A.* 52, 128) converted it by chromic mixture into propionic acid (called therefore Metacetonic acid). Benedikt (*A.* 162, 303) found V.D. 3·53 instead of 3·59, and stated that it did not combine with $NaHSO_3$. Meta-acetone has also been examined by Favre (*A. Ch.* [3] 11, 80), Cahours (*C. R.* 30, 319), who describes it as present in crude wood spirit, Lies-Bodart (*J.* 1856, 455), and Schwartz (*J.* 1850, 533). Nevertheless Pinner (*B.* 15, 586; 16, 1729) considers metacetone to be a very complicated mixture. H. W.

Para-acetone *v.* PINACONE.

ACETONE-ALCAMINES. — These are products derived from the acetonamines by reduction, their CO being converted into CH(OH).

Diacetone-alcamine $C_6H_{15}NO$ *i.e.* $NH_2.CMe_2.CH_2.CH(OH).Me$ (175°). Formed by reduction of diacetonamine by gradually adding sodium-amalgam to its solution in alcohol diluted with aqueous ammonia. Liquid, having a faint ammoniacal odour, miscible in all proportions with water. Absorbs CO_2 from the air; fumes with HCl. $(C_6H_{15}NOHCl)_2PtCl_4$ forms orange-red triclinic crystals, easily soluble in hot water.

Ethylidene-diacetone-alcamine

$C_8H_{17}NO$ *i.e.*
```
H2C – CH(OH) – CH2
 |              |
MeHC  —  NH  — CMe2
```

Oxy-tri-methyl-hexa-hydro-pyridine [123°]. Colourless crystalline solid. Easily soluble in water and alcohol, sparingly in ether, and ben[illegible]. Formed by reduction of ethylidene-$C_7H_{15}NO$,H[illegible]ine with sodium-amalgam in slightly cold, v. sol. hot, solution. The hydro-chloride *normal oxalate* (C[illegible]dles, the sulphate large flat [illegible]inct very deliquescen[illegible]7, 1794). absolute alcohol; the *aci*[illegible] $C_8H_{19}NO$ crystallises in small pris[illegible]–CH_2 alcohol. The *picrate* for[illegible] [128·5°] (Götschmann, *A.* 197, 38). [illegible]Me$_2$

Dimethyldiacetonamine [illegible]*ine.* Formed $C_8H_{17}NO$ *i.e.* $CO Me.CH_2.CMe_2$ [illegible] by reduc- is formed on heating a solution of [illegible]algam in mine in acetone at 100°–105° in a se[illegible]ars, *B.* 17[illegible] Free dimethyldiacetonamine has not [illegible] this tained as it very easily splits up into dim[illegible]e to amine and mesityl oxide. The *platino-ch*[illegible] be $(C_8H_{17}NOHCl)_2PtCl_4$ crystallises in small tabl[illegible]

forms rhombic crystals (Heintz, *A.* 183, 200, 317).

Methyl-tri-acetone-alcamine $C_{10}H_{21}NO$ [74°] or, when hydrated, [60°]. Formed from tri-acetone-alcamine by MeI and MeOH at 100° (E. Fischer, *B.* 16, 1605). Slender plates (from water). Strongly alkaline. H. W.

ACETONE ALCOHOL *v.* ACETYL-CARBINOL.

ACETONE-AMMONIA *v.* ACETONAMINES.

ACETONE-BENZIL $C_{17}H_{16}O_3$ *i.e.*

$Ph.CO.CPh(OH).CH_2.CO.CH_3$ [78°].

Preparation.—Benzil is shaken with excess of pure acetone and a little conc. KOH, and the crystals obtained are dissolved in ether (free from alcohol), which is allowed to evaporate. $C_{14}H_{10}O_2 + C_3H_6O = C_{17}H_{16}O_3$ (Japp a. Miller, *C. J.* 47, 21).

Properties.—Colourless square prisms. Sol. ether or alcohol. Resolved by heat into its constituents.

Reactions.—1. *Chromic mixture* gives benzoic and acetic acids.—2. Dry NH_3 gives *acetone-benzilimide* (*q. v.*).—3. Alcoholic *hydroxylamine* gives $C_{17}H_{16}O_2(NOH)$, [146°]; m. sol. benzene, sl. sol. ether. This body is not affected by further treatment with hydroxylamine.

Dehydro-acetone-benzil $C_{17}H_{14}O_2$ *i.e.*

```
             CH2
            /   \
Ph.CO.CPh<       >CO   [149°].
            \   /
             CH2
```

Preparation.—Benzil is shaken with excess of pure acetone and excess of conc. KOH (J. a. M.) $C_{14}H_{10}O_2 + C_3H_6O = C_{17}H_{14}O_2 + H_2O$.

Properties.—Colourless prisms.

Reactions.—1. Converted by *bromine* in chloroform to a bromo derivative, $C_{17}H_{13}BrO_2$ [172°]; slender needles (from glacial HOAc).—2. *Chromic acid* in glacial HOAc forms an acid, $C_{16}H_{14}O_3$, [152°]; needles. Salts, AgA′—BaA′$_2$ 2aq.

Dehydro-acetone-di-benzil $C_{31}H_{24}O_4$ [195°].

Formation.—1. From acetone-benzil and dilute alcoholic KOH.—2. From acetone, excess of benzil, and a little conc. KOH.

$$2C_{14}H_{10}O_2 + C_3H_6O = C_{31}H_{24}O_4 + H_2O.$$

Properties.—Colourless crystals (from benzene); sl. sol. boiling alcohol. Crystallises from alcohol with one molecule EtOH.

ACETONE-BENZILIMIDE $C_{17}H_{17}NO_2$ [176°]. From acetone-benzil and dry NH_3. Flat plates (from alcohol). Heated with HCl and oxalic acid, gives a red gum (J. a. M.).

ACETONE-BORIC ACID *v.* ACETONE.

ACETONE-BROMIDE = DI-BROMO-PROPANE (*q. v.*).

ACETONE-BROMOFORM $C_4H_7OBr_3$ *i.e.* $Me_2C(OH).CBr_3$ [175°], or, when hydrated [167°]. From bromoform (5g.), acetone (30g.), and soda-lime (8g.) (Willgerodt a. A. Müller, *C. C.* 1884, 808).

ACETONE CARBOXYLIC ACID = ACETO-ACETIC ACID (*q. v.*).

Acetone di-carboxylic acid $C_5H_6O_5$ *i.e.* $CO_2H.CH_2.CO.CH_2CO_2H$ [c. 130°]. Formed by heating citric acid with H_2SO_4. Colourless needles. Split up into CO_2 and acetone by heat, by boiling water, or by warm acids or alkalis. It contains methylenic hydrogen displaceable by Na. Fe_2Cl_6 gives a violet colour. It reacts with phenyl-hydrazine (Pechmann, *B.* 17, 2542). It forms a compound with HCN, [illegible] 69), which on saponification produces citric acid.

$NaNO_2$ converts it into di-oximido-acetone (Pechmann a. Wehsarg, *B.* 19, 2465).

The **ethyl ether** is an oil which can give rise to salts by exchanging its methylenic hydrogen for sodium or copper. *Reactions.*—1. By successive treatment with sodium and an alkyl iodide (RI) the following ethers may be got: $CO_2Et.CH_2.CO.CHR.CO_2Et$, $CO_2Et.CHR.CO.CHR.CO_2Et$, $CO_2Et.CHR.CO,CR_2.CO_2Et$, and finally $CO_2Et.CR_2.CO.CR_2.CO_2Et$. The acids obtained by saponifying these bodies are split up by heat into CO_2 and alkyl-acetones (Dünschmann a. v. Pechmann, *B.* 18, 2289).—2. Acetone di-carboxylic ether (100 g.) is converted by heating with Na (21 g.) into di-oxy-phenyl-acetic di-carboxylic ether $C_6H(OH)_2(CO_2Et)_2.CH_2.CO_2Et$ (Cornelius a. Pechmann, *B.* 19, 1446).—3. Ammonia produces β-oxy-β-amido-glutaramic ether, $CO_2Et.CH_2.C(OH)(NH_2).CH_2.CO.NH_2$ [86°] (v. Pechmann a. Stokes, *B.* 18, 2290; 19, 2694).

ACETONE CHLORIDE *v. di*-Chloro-propane.

ACETONE CHLOROFORM $C_4H_7OCl_3$ *i.e.* $Me_2C(OH).CCl_3$. *Oxy-iso-butyro-tri-chloride.* [96°] or when hydrated, + ½aq, [81°] (167° uncor.). Prepared by adding solid KOH to a cold mixture of acetone and chloroform. It is a crystalline solid, resembling camphor in appearance and smell. Rotates on water. V. sol. alcohol, ether, chloroform, acetone, or glacial HOAc, insol. water. Volatile with steam. Converted by water at 180° into α-oxy-iso-butyric acid (Willgerodt, *B.* 14, 2451; 15, 2305; 16, 1585).

ACETONE CYANHYDRIN *v.* Acetone.

ACETONE-HYDROQUINONE $C_9H_{12}O_3$. From acetone and hydroquinone (Habermann, *M.* 5, 329).

ACETONE HYDROXYLAMIDE *v.* Acetoxim.

ACETONE-PHENANTHRAQUINONE $C_{17}H_{14}O_3$ [90°].

Formation.—From phenanthraquinone by heating with a large excess of acetone at 200°. The product is washed with $NaHSO_3$ and extracted with ether (Japp a. Streatfeild, *C. J.* 41, 274).

Preparation.—Phenanthraquinone (50 g.) is shaken in a glass with acetone (60 g.) and conc. NH_3Aq(40 c.c.). Acetone-phenanthraquinonimide is formed and filtered off; after washing with ether, it is made into a cream with water and stirred into a solution of oxalic acid (90 g.) in water (800 c.c.) at 25°. The substance dissolves, but minute needles of acetone-phenanthraquinone soon separate (Japp a. Miller, *C. J.* 47, 18).

Properties.—Large thin blades (from ether). Insol. water, v. sol. ether, acetone or alcohol.

Reactions.—1. By *heat*, by *boiling water*, or by *boiling alcohol*, it is resolved into acetone and phenanthraquinone: $C_{17}H_{14}O_3 = C_{14}H_8O_2 + C_3H_6O$. 2. *Zinc dust* and glacial HOAc form $C_{17}H_{12}O$, [121°]. This is extracted by ether and crystallised from alcohol. It forms long slender needles, v. e. sol. ether or chloroform, v. sol. boiling alcohol, v. sl. sol. cold alcohol. Sublimes in feathery crystals. It decolorises bromine.—3. A few drops of dilute aqueous KOH added to an alcoholic solution forms minute crystals of acetone-di-phenanthraquinone (*q. v.*).—4. Conc. KOH (S.G. 1·27) added to a solution of acetone-phenanthraquinone in acetone forms a crystalline mass of di-acetone-phenanthraquinone.—5. *Ammonia* passed into an ethereal solution of acetone-phenanthraquinone forms crystals of acetone-phenanthraquinonimide.

Acetone-di-phenanthraquinone $C_{31}H_{22}O_5$ [190°]. Formed by adding a little dilute KOH to an alcoholic solution of acetone-phenanthraquinone (J. a. M.): $2C_{17}H_{14}O_3 = C_{31}H_{22}O_5 + C_3H_6O$. Colourless crystals (from benzene).

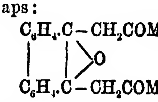
Di-acetone-phenanthraquinone $C_{20}H_{20}O_4$ [187°].

Preparation.—Pure acetone (43 g.) is shaken with finely powdered phenanthraquinone (50 g.) and a little (2 c.c.) conc. KOHAq (S.G. 1·27). After 12 hrs. the resulting solid cake is washed with ether and crystallised from acetone (J. a. M.).

Properties.—Short oblique prisms. Sparingly soluble in the usual menstrua. Sol. acetone or benzene. Decomposed by boiling glacial HOAc or amyl alcohol. Decomposed on melting into acetone and phenanthraquinone.

Reactions.—Boiling Ac_2O converts it into dehydro-di-acetone-phenanthraquinone.

Dehydro-di-acetone-phenanthraquinone $C_{20}H_{18}O_3$ [179°-181°]. Colourless pointed prisms (from benzene). Formed as above. Its constitution is perhaps:



Dehydro-acetone-phenanthraquinone $C_{17}H_{12}O_2$ [195°]. Formed in small quantity, together with di-acetone-phenanthraquinone when excess of KOHAq (S.G. 1·27) acts upon a mixture of acetone and phenanthraquinone. It is present in the ethereal washings of the di-acetone-phenanthraquinone (J. a. M.).

Groups of minute needles (from benzene): m. sol. hot benzene, hot alcohol, or ether.

Acetone-phenanthraquinonimide $C_{17}H_{15}NO_2$ [130°]. *Formation.*—By passing NH_3 into an ethereal solution of acetone-phenanthraquinone.

Preparation.—Phenanthraquinone (50 g.), acetone (60 g.), and conc. NH_3Aq (40 c.c.), shaken together form a white crystalline powder which is washed with ether and crystallised from acetone containing a little NH_3Aq:

$$C_{14}H_8O_2 + C_3H_6O + NH_3 = C_{17}H_{15}NO_2 + H_2O$$

(J. a. S.). Colourless rhomboidal laminæ.

Reactions.—1. Ac_2O decomposes it, forming phenanthraquinone.—2. Cold conc. HCl dissolves it, but the solution soon deposits a dark blue substance. The diluted filtrate deposits colourless needles of acetone-phenanthraquinone:

$$C_{17}H_{15}NO_2 + H_2O = C_{17}H_{14}O_3 + NH_3$$

By using conc. aqueous oxalic acid as a solvent the formation of the blue compound may be avoided, and after dilution, the needles separate as before.

The following constitutional formulæ are suggested by Japp and Miller to explain the properties of the preceding bodies:

$C_6H_4.C(OH).CH_2.CO.Me$
$C_6H_4.CO$ for $C_{17}H_{14}O_3$

$C_6H_4.C(OH).CH_2.CO.Me$
$C_6H_4.C:NH$ for $C_{17}H_{15}NO_2$

$C_6H_4.C(OH).CH_2.CO.Me$
$C_6H_4.C(OH).CH_2.CO.Me$ for $C_{20}H_{20}O_4$

ACETONE-PHENYL-HYDRAZIDE: $(CH_3)_2C$:N.NHPh (165°) at 91 mm. Oil. Prepared by mixing acetone with phenyl-hydrazine. It dissolves in cold aqueous acids and on warming the solution it is resolved into its constituents (Reisenegger, *B.* 16, 662).

DI-ACETONE-PHOSPHINIC ACID $C_6H_{13}PO_4$ aq, *i.e.* $(CH_3)_2CH.CHAc.PO(OH)_2$ aq, or, less probably $(CH_3.CO.CH_2)_2PH(OH)_2$aq. *Di-acetonyl-phosphinic acid, iso-propyl-acetonyl-phosphonic acid, ω-acetyl-iso-butane ω-phosphonic acid* [64°]. Formed by the action of water upon di-acetone-phosphorous chloride (*infra*). (Michaelis, *B.* 17, 1273; 18, 902):

$$C_6H_{10}O_2PCl + 2H_2O = C_6H_{13}PO_4 + HCl.$$

Slender needles. V. e. sol. water or alcohol, v. sol. ether. Strong dibasic acid.

Salts.—NH_4HA''. V. sol. water, sl. sol. alcohol. Crystals.—$(NH_4)_3HA''_2$ 2aq. Insol. alcohol. —$BaH_2A''_2$ 2aq. Needles; v. sol. water, sl. sol. alcohol.—BaA″ 6aq; m. sol. hot water; trimetric tables, $a : b : c = \cdot785 : 1 : 2\cdot525$.—PbA″.—PbA″ $\frac{1}{2}$ PbO.—MgA″ 6aq; ppd. by alcohol from aqueous solution in glittering plates. —KHA″; deliquescent gum: v. sol. alcohol.—$KH_3A''_2$; slender needles, v. sol. water, sl. sol. alcohol.—Ag_2A''.

Reactions.—1. HNO_3 forms a tribasic crystalline acid $C_4H_9PO_5$, possibly β-carboxy-propane-phosphonic acid: $CH_3.CH(CO_2H).CH_2.PO(OH)_2$. The salts Ag_3A''', and $Ba_3A'''_2$, are crystalline.

Oxim.—$C_6H_{12}(NOH)PO_3$ [170°]. Colourless crystals; v. sol. water or alcohol; dibasic acid.

Di-Acetone-phenyl-phosphinic Acid $C_6H_{12}(C_6H_5)PO_3$, probably $(CH_3)_2CH.CH(CO.CH_3).PO(C_6H_5)OH$. [86°]. Prepared by adding P_2O_5 to a mixture of acetone and phosphenyl chloride, and treating the product with water:

(1) $2C_3H_6O + C_6H_5PCl_2 - H_2O = C_6H_{10}(C_6H_5)POCl_2$

(2) $C_6H_{10}(C_6H_5)POCl_2 + 2H_2O = C_6H_{12}(C_6H_5)PO_3 + 2HCl.$

Long colourless plates (+H_2O). Sol. hot water, sl. sol. cold water and ether, v. e. sol. alcohol. The anhydrous acid forms a glassy mass, v. sol. ether. A′Ag; crystals, v. sol. water. (Michaelis, *B.* 19, 1009.)

Di-Acetone-*p*-tolyl-phosphinic Acid $C_6H_{12}(C_7H_7)PO_3$, probably $(CH_3)_2CH.CH(CO.CH_3).PO(C_7H_7)OH$. [103°]. Obtained by adding P_2O_5 to a mixture of acetone and *p*-tolyl-phosphorous chloride, and treating the product with water. Glistening plates; sol. hot water, v. sol. alcohol and ether. A′Ag; slender glistening soluble needles. (Michaelis, *B.* 19, 1012.)

DI-ACETONE-PHOSPHORIC-TRI-CHLORIDE

$$C_6H_{10}O_2PCl_3 \text{ i.e. } \begin{array}{c}(CH_3)_2{:}C - O\\ |\quad\quad | \\ CH_3.CO.CH - PCl_3\end{array} \ (?)$$

[115°]. Formed by passing chlorine into a solution of di-acetone-phosphorous chloride in petroleum-ether (Michaelis, *B.* 18, 901). Colourless crystals; sl. sol. petroleum-ether.

DI-ACETONE-PHOSPHORIC-CHLORO-BROMIDE

$$C_6H_{10}O_2PClBr_2 \text{ i.e. } \begin{array}{c}(CH_3)_2C - O\\ |\quad\quad | \\ CH_3.CO.CH - PClBr_2\end{array} \ (?)$$

[142°]. Formed by addition of bromine to a solution of di-acetone-phosphorous chloride in light petroleum (Michaelis, *B.* 18, 900). Colourless crystals. Sl. sol. light petroleum. It is decomposed by water into mesityl oxide, phosphoric acid, HCl, and HBr.

ACETONE-PHOSPHOROUS ACID *v.* ACETONE.

DI-ACETONE-PHOSPHOROUS CHLORIDE

$$C_6H_{10}O_2PCl \text{ i.e. } \begin{array}{c}(CH_3)_2C - O\\ |\quad\quad | \\ CH_3.CO.CH.PCl\end{array} \ (?)$$

[36°]. (154°) at 100 mm.; (235°) at 745 mm. S.G. (liquid) $\frac{17}{17}$ 1·209. Prepared by slowly adding Al_2Cl_6 (8 pts.) to a cooled mixture of PCl_3 (50 pts.) and $2\frac{1}{2}$ times its volume of acetone; yield: 5 pts. It is decomposed by water into di-acetone-phosphinic acid $C_6H_{13}PO_4$ and HCl. It readily combines with 1 mol. of chlorine or bromine (Michaelis, *B.* 17, 1273; 18, 898).

ACETONE SULPHONIC ACID *v.* ACETONE.

ACETONIC ACID *v.* α-OXY-ISO-BUTYRIC ACID.

DI-ACETONIC ALCOHOL *v.* ACETYL-BUTYL ALCOHOL.

ACETONINE $C_9H_{18}N_2$. This base described by Städeler (*A.* 111, 277), Hlasiwetz (*A.* 76, 294), and Mulder (*A.* 168, 228), was found by Heintz (*A.* 201, 102) to be a mixture of di-acetonamine, tri-acetonamine, and tri-acetone-di-amine.

ACETONINES. Bases obtained by dehydrating acetone-alcamines by conc. H_2SO_4.

Ethylidene-di-acetonine $C_8H_{15}N$ *i.e.*

$$\begin{array}{c}CH{:}CH.CH_2\\ |\quad\quad\quad | \\ MeCH.NH.CMe_2\end{array} \text{ or } \begin{array}{c}CH_2CH{:}CH\\ |\quad\quad\quad | \\ MeCH.NH.CMe_2\end{array}$$

Tri-methyl-tetra-hydro-pyridine. (132°–137°.) Formed from ethylidene-di-acetone-alcamine (1 pt.) and conc. H_2SO_4 (3 pts.) by heating for $1\frac{1}{2}$ hours at 100°.

Colourless oil with alkaline reaction. Volatile with steam. Sl. sol. water, more soluble in cold than in hot water. Miscible with alcohol, ether, or chloroform. Heated with HI, it yields iodo-tri-methyl-piperidine, $C_5H_7Me_3IN$ [60°].

Salts.—B′HI; slender, sparingly soluble needles.—B′HBr; small soluble trimetric pyramids (Fischer, *B.* 17, 1795).

Benzylidene-di-acetonine $C_{13}H_{17}N$ *i.e.*

$$\begin{array}{c}H_2C - CH = CH\\ |\quad\quad\quad\quad | \\ PhHC - NH - CMe_2\end{array} \text{ or } \begin{array}{c}HC = CH - CH_2\\ |\quad\quad\quad\quad | \\ PhHC - NH - CMe_2.\end{array}$$

Phenyl-di-methyl-tetra-hydro-pyridine. Formed by the action of strong H_2SO_4 on benzylidene-di-acetone-alcamine.

Distils undecomposed. Volatile with steam. V. sol. alcohol or ether, v. sl. sol. water.

Salts.—*B′HBr: colourless tables or needles, sl. sol. cold water.—B′HI; sparingly soluble needles.—*$B'HAuCl_4$. (Fischer, *B.* 17, 1797.)

Tri-acetonine

$$C_9H_{17}N \text{ i.e. } \begin{array}{c}H_2C.CH{:}CH\\ |\quad\quad\quad | \\ Me_2C.NH.CMe_2\end{array} \ (146°) \text{ at } 740 \text{ mm.}$$

Tetra-methyl-tetra-hydro-pyridine.

Prepared by heating tri-acetone-alcamine (1 pt.) with strong H_2SO_4 (3 pts.) on a water-bath for an hour, pouring into water, neutralising the acid, and distilling the base over with steam (Fischer, *B.* 16, 1604).

Properties.—Mobile fluid, smelling like piperidine. It combines with water forming a hydrate crystallising in long white needles, which give off their water at a moderate temperature. Volatile with steam. Poisonous. By heating with HI it gives iodo-tetra-methyl-piperidine.

Salts.—B′HBr; large white prisms, sl. sol. cold water.—B′HCl; v. sol. water or alcohol.—$B'HAuCl_4$; yellow needles.

Nitrosamine $C_9H_{16}N(NO)$: yellowish tables; v. sol. alcohol, ether, and benzene, nearly insoluble in water; volatile with steam; strong camphor-like smell.

Methyl derivative $C_9H_{16}NMe$: colourless oil very volatile with steam, sparingly soluble in water (Fischer, *B.* 17, 1789).

ACETO-NITRANILIDE *v.* NITRO-ANILINE.

ACETONITRILE C_2H_3N *i.e.* $CH_3.C{:}N$. *Methyl cyanide, methyl isocyanide.* M.w. 41. (81·6°) at 760 mm. (Vincent a. Delachanal, *Bl.* 33, 405); (81·3°) (R. Schiff, *B.* 19, 567). S.G. $\frac{0}{0}$ ·805; $\frac{15}{15}$ ·789 (V. a. D.). S.V. 57·23 (S.). H.F.p. −15,680. H.F.v. −16,260 (Thomsen). μ_D 1·3458 (V. a. D.). R_∞ 18·00 (Kanonnikoff, *J. pr.* [2] 31, 361). V.D. 1·45 (for 1·42).

Occurrence.—In crude benzene (V. a. D.).

Formation.—1. Dry $KMeSO_4$ is distilled with dry KCN and the distillate rectified over $CaCl_2$ (Frankland a. Kolbe, *C. S. Mem.* 3, 386; *A.* 65, 288).—2. From Me_2SO_4 and KCN, the product being distilled over HgO and then over P_2O_5 (Dumas, Malaguti a. Leblanc, *C. R.* 25, 474).—3. By distilling NH_4OAc with P_2O_5 (Dumas, *C. R.* 35, 383).—4. By distilling acetamide with P_2O_5 (Buckton a. Hofmann, *C. J.* 9, 242).—5. By distilling acetamide (5 mols.) with P_2S_5 (1 mol.), washing the product with NaOHAq and digesting with PbO (Henry, *A.* 152, 149).—6. From acetamide by action of PCl_5 (Wallach, *A.* 184, 21).

Preparation.—1. By boiling acetamide (500 g.) for a week with a little glacial acetic acid, the water produced being constantly allowed to distil off. The theoretical yield is got (Demarçay, *Bl.* [2] 33, 456).

Properties.—Colourless liquid with a pleasant ethereal odour; burns with a reddish-bordered flame. Miscible with water, but separated by salts from the solution. Mixes with alcohol. The presence of a little alcohol lowers its boiling-point several degrees (D.).

Reactions.—1. Hot aqueous KOH acts thus:
$CH_3.CN + H_2O + KOH = CH_3CO_2K + NH_3$.
2. *Chromic* and *nitric* acids have no action.—3. Heated with Na, it forms CYANMETHINE (*q.v.*) and NaCN.—4. Glacial HOAc at 200° forms di-acetamide: $CH_3CN + CH_3.CO.OH = (CH_3.CO)_2NH$ (Gautier, *A.* 150, 189).—5. Ac_2O, forms triacetamide: $CH_3.CN + (CH_3.CO)_2O = (CH_3.CO)_3N$. 6. Combines with dry HBr, HI, and (with difficulty) with HCl (Gautier, *A.* 142, 291).—7. *Bromine* forms the hydrobromide of the nitrile of BROMO-ACETIC ACID (*q.v.*), $CH_2Br.CH{:}NBr$ [65°].

Combinations.— C_2H_3N2HBr, or $CH_3.CH_2.NBr_2$ [47°–50°] crystals; may be sublimed.—$C_2H_3NPCl_5$ (72°); dissociated above its boiling point (Hencke, *A.* 106, 281).—$C_2H_3NSbCl_5$, formed with great rise of temperature; white crystals which may be sublimed (H.).—$C_2H_3NAuCl_3$: brownish-yellow powder (H.).—$(C_2H_3N)_2TiCl_4$: white crystalline crusts; may be sublimed (H.).—$(C_2H_3N)_2SnCl_4$: sublimes in arborescent formations (H.).—$C_2H_3N2Hg(CN)_2$: white vitreous mass; decomposes even over H_2SO_4 (Hesse, *A.* 110, 202), $CH_3.C(NH_2){:}NOH$, formed by the union of aceto-nitrile with hydroxylamine *v.* ETHENYL-AMID-OXIM.

ACETONURAMIC ACID $C_5H_{10}N_2O_3$ *i.e.* $NH_2.CO.NH.CMe_2.COOH$. *a-Uramido-iso-butyric acid, di-methyl-hydantoic acid.* Obtained, as barium salt $(C_5H_9N_2O_3)_2Ba(OH)_2$, by prolonged boiling of a solution of di-methyl-hydantoïn with baryta-water. The acid itself appears to be very unstable (Urech, *A.* 164, 255). A more stable acid of the same composition is obtained by evaporating the mixed solutions of the sulphate of amido-isobutyric acid and potassium cyanate. It forms crystals, melting, with loss of water, at 160°, moderately soluble in hot water and alcohol. Decomposed by prolonged heating at 130°–140° into water and di-methyl-hydantoïn. $C_5H_9AgN_2O_3$ crystallises in needles (Urech, *A.* 164, 274). H. W.

ACETONYL-ACETO-ACETIC ETHER $C_9H_{14}O_4$, *i.e.* $CH_3.CO.CH_2.CHAc.CO_2Et$, *a-β-di-acetyl propionic ether.*

From aceto-acetic ether and chloro-acetone (Weltner, *B.* 17, 67). Liquid. Warm conc. HCl changes it to pyrotritaric ether $C_7H_7O_3Et$. Water at 160° produces some acetonyl-acetone.

ACETONYL-ACETONE $C_6H_{10}O_2$ *i.e.* $CH_3.CO.CH_2.CH_2.CO.CH_3$. *Di-methylethylene di-ketone.* (188° uncor.)

Formation.—(1) By heating pyrotritaric acid (di-methyl-furfurane-carboxylic acid) with water at 150°–160°; yield nearly theoretical. (2) By heating acetonyl-aceto-acetic ether with water at about 160°; small yield.

Properties.—Mobile liquid of peculiar smell. Miscible with water, alcohol, and ether, insol. conc. KOHAq, or K_2CO_3Aq.

Reactions.—P_2S_5, when heated with it, forms thioxene C_6H_8S.—Heating with alcoholic NH_3 gives di-methyl-pyrrol (Paal, *B.* 18, 2251); *amines* behave similarly (Paal a. Schneider, *B.* 19, 3156).

Di-oxim $CH_3.C(NOH).CH_2.CH_2.C(NOH).CH_3$ [135°]. White glistening plates, v. sol. hot water, alcohol, or ether, v. sl. sol. benzene.

Di-phenyl-di-hydrazide $C_2H_4(CMe{:}N_2HPh)_2$ [120°]: plates, v. sol. alcohol, ether, or benzene, nearly insol. light petroleum (Paal, *B.* 18, 58).

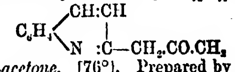
ACETONYL-CARBAMATE $C_4H_7NO_3$ [76°]. Formed by boiling acetonyl thiocarbamate (*infra*) with lead acetate or silver oxide. Crystallises from water in prisms, may be distilled; dissolves in water, alcohol, and ether. Decomposed by heating with strong hydrochloric acid or baryta-water, yielding CO_2, NH_3, and a-oxy-iso-butyric acid. The salts $C_5H_8AgNO_3$, and $AgNO_3.2C_5H_7NO_3$ are crystalline (Urech, *B.* 11, 467; 13, 485). H. W.

ACETONYL-PHOSPHINIC ACID $C_3H_7PO_3$ *i.e.* $CH_3.CO.CH_2.P(OH)_2$. Residue left after distilling acetone with I and P (*v. Acetone-phosphorous acid* under ACETONE). *Salt.*—$Ba(C_3H_6PO_3)_2$.

Di-acetonyl phosphinic Acid *v.* DI-ACETONE-PHOSPHINIC ACID.

Di-acetonyl-phosphorous Chloride *v.* DI-ACETONE-PHOSPHOROUS CHLORIDE.

ACETONYL-QUINOLINE $C_{12}H_{11}NO$ *i.e.*



Quinolyl-acetone. [76°]. Prepared by reducing *o*-nitro-cinnamoyl-acetone in alcoholic solution with $SnCl_2$. Long yellow needles. Distils without decomposition. Sparingly volatile with steam. Insol. cold water, sl. sol. hot water. Dyes wool and silk yellow. Heated with strong HCl at 170° it gives (*Py.* 3)-methyl-quinoline (Fischer a. Kuzel, *B.* 16, 163).

ACETONYL-THIO-CARBAMATE (so called) $C_4H_7NSO_2$. *Thiacetonuramic acid.* [152°].

Formed by treating acetone with a mixture of potassium cyanide and sulphocyanide, and HCl: $C_3H_6O + CNH + CNSH + H_2O = NH_3 + C_5H_7NSO_2$. Long needles; easily sublimable; very soluble in ether; less easily in cold water. Resolved by heating with HCl in a sealed tube at 120° into CO_2, H_2S, NH_3, and α-oxy-iso-butyric acid. The silver salt $C_5H_6AgNSO_2$ is very sparingly soluble (Urech, *B.* 6, 1117). H. W.

ACETONYL-UREA *v.* DI-METHYL HYDANTOÏN.

ACETO-PHENINE *v.* ACETOPHENONE, *Reaction* 6.

ACETO-PHENONE C_8H_8O *i.e.* $C_6H_5.CO.CH_3$. *Phenyl methyl ketone, Acetyl-benzene.* M. w. 120. [20·5°]. (202° cor.). S. G. $\frac{15}{}$ 1·032.

Formation.—1. By distilling calcium benzoate with calcium acetate (Friedel, *A.* 108 122).—2. From BzCl and $ZnMe_2$ (Popoff, *A.* 161, 296).—3. By action of KOHAq on benzoyl-aceto-acetic ether. — 4. From phenyl-acetylene by shaking with diluted (75 p.c.) H_2SO_4 (Friedel a. Balsohn, *Bl.* [2] 35, 54): $Ph.C⋮CH + H_2O = Ph.CO.CH_3$.—5. From bromo-styrene and H_2SO_4: small yield.—6. Bromo-styrene heated with a large excess of water for 12 hours at 180° yields 66 per cent. (Friedel a. Balsohn, *Bl.* [2] 32, 613).—7. From ethyl-benzene and chromic acid in acetic acid (F. a. B.).—8. From di-bromo-phenyl-propionic acid, $CH_2Br.CBrPh.CO_2H$ by boiling water (Fittig a. Wurster, *A.* 195, 160).

Preparation.—From benzene (10 pts.), acetyl chloride (1 pt.), and $AlCl_3$ (2 pts.) (Richter).

Properties.—Large plates. Does not combine with $NaHSO_3$ but, like other ketones, it reacts with hydroxylamine, phenyl-hydrazine, and HCN.

Reactions.—1. *Chromic-mixture* oxidises it to benzoic and carbonic acids (Popoff).—2. *Sodium-amalgam* reduces it to phenyl methyl carbinol, $CH_3.CHPh.OH$, and acetophenone-pinacone.—3. With HI and P at 140° it gives di-phenyl-di-methyl-ethane, $C_{16}H_{18}$, and a compound $C_{16}H_{16}O$ (Graebe, *B.* 7, 1626; *v.* ACETOPHENONE-PINACOLINE).—4. *Chlorine* produces chloro-acetophenone $Ph.CO.CH_2.Cl$ [59°] (245°) and di-chloro-acetophenone $Ph.CO.CHCl_2$ (250°-255°) *v.* CHLORO-ACETOPHENONE.—5. *Bromine* in CS_2 produces bromo-acetophenone, $Ph.CO.CH_2Br$ [50°] *v.* BROMO-ACETOPHENONE.—6. *Ammonia* in presence of P_2O_5 forms 'acetophenine' $C_{24}H_{17}N$ together with methane. Acetophenine crystallises from alcohol in slender needles, which may be sublimed. It is a weak base; its hydrochloride crystallises in plates, decomposed by water into HCl and the base. Fuming HNO_3 forms tri-nitro-acetophenine $C_{23}H_{14}(NO_2)_3N$; slender needles (from ether). Acetophenine is probably tri-phenyl-pyridine:

```
  CPh:CH
N<        >CPh
  CPh.CH
```

(Engler a. Riehm, *B.* 19, 40).—7. When taken internally it reappears in the urine as hippuric acid, having, doubtless, been previously oxidised as in *Reaction* 1 (M. Nencki, *J. pr.* 123, 288).

Besides the derivatives described below, see also: AMIDO-ACETOPHENONE, BROMO-ACETOPHENONE, BROMO-NITRO-ACETOPHENONE, IODO-ACETOPHENONE, DI-METHYL-AMIDO-ACETOPHENONE, NITRO-ACETOPHENONE, THIO-ACETOPHENONE, ACETOPHEN-OXIM.

ACETOPHENONE-ACETO-ACETIC ACID $C_{12}H_{12}O_4$ *i.e.* $CH_3.CO.CH(CO_2H).CH_2CO.C_6H_5$ *Acetophenone-acetone-carboxylic acid* [130°-140°]. Small colourless crystals. Obtained by saponification of the ether which is prepared by the action of ω-bromo-acetophenone on sodio-aceto-acetic ether. It is very unstable. On warming with absolute alcohol it evolves CO_2 and yields acetophenone-acetone $CH_3.CO.CH_2.CH_2.CO.C_6H_5$ (Paal, *B.* 16, 2865). Acetophenone-aceto-acetic ether is reduced by sodium amalgam to a oily lactone, $CH_3.CH.CH_2.CH(CHMeOH).CO.O$, sol. aqueous KOH or $Ba(OH)_2$ but insol. aqueous K_2CO_3 (Weltner, *B.* 17, 69). *Amines* convert acetophenone aceto-acetic ether into derivatives of pyrrol (Paal a. Schneider, *B.* 19, 3156).

Dehydro-acetophenone-aceto-acetic acid $C_{12}H_{10}O_3$ [114°]. From acetophenone-aceto-acetic ether $C_6H_5.CO.CH_2.CH(CO_2Et).CO.CH_3$ by heating with alcoholic KOH. Large crystals (from benzene mixed with benzoline). From dilute alcohol it separates in hydrated needles [115°-120°]. By boiling with HCl it is converted into phenyl-methyl-furfurane-carboxylic acid

```
   HC  C(CO2H)
   //    \\
PhC—O—CMe.
```

Salts.—KA'. Long silky needles (from alcohol). NH_4A'.

Oxim $C_{12}H_{12}N_2O_3$: [172°]; glistening white plates; sparingly soluble in water, easily in alcohol, ether, benzene, aqueous acids, and alkalis.

Phenyl-hydrazide $C_{18}H_{16}N_2O_2$: small needles (Paal, *B.* 17, 916, 2761).

ACETOPHENONE-ACETONE $C_{11}H_{12}O_2$ *i.e.* $CH_3.CO.CH_2.CH_2.CO.C_6H_5$ (*acetyl-benzoyl-ethane* or *ethylene methyl phenyl di-ketone*). Prepared by heating acetophenone-aceto-acetic acid (*q.v.*) with absolute alcohol. Yellowish heavy oil. Sl. sol. water, quite insol. alkalis. Cannot be distilled (Paal, *B.* 16, 2868).

Reactions.—1. P_2O_5 removes H_2O forming phenyl-methyl-furfurane,

```
 CH--CH
 ||   ||
MeC.O.CPh.
```

2. Heated with P_2S_5 it gives, similarly, phenyl-methyl-thiophene,

```
 CH—CH
 ||   ||
MeC.S.CPh.
```

3. Heated with alcoholic NH_3 it gives, similarly, phenyl-methyl-pyrrol,

```
 CH--CH
 ||   ||
MeC.NH.CPh
```

(Paal, *B.* 18, 367).

Oxim $C_{11}H_{13}NO_2$. [123°]. Formed by action of hydroxylamine. Long white needles, soluble in acids or alkalis.

Phenyl-hydrazide $C_{17}H_{18}N_2O$ [c. 105°]. White prisms, got by adding phenyl-hydrazine slowly to a solution of the ketone in ether (3 vols.). V. sol. ether or benzene, nearly insoluble in light petroleum (Paal, *B.* 17, 2763).

$C_{17}H_{16}N_2$ [155°]. Formed by mixing the ketone with phenyl-hydrazine (cf. Knorr, *B.* 18, 305).

Dehydro-acetophenone-acetone $C_{11}H_{10}O$. [83°]. This body is formed together with the isomeric phenyl-methyl-FURFURANE by the action of Ac_2O and other dehydrating agents upon acetophenone-acetone. Cannot be distilled, even with steam. It combines with bromine, and gives with phenyl-hydrazine the same compound,

$C_{17}H_{16}N_2$ [155°], that the acetophenone-acetone itself gives. Hence its constitution must be something like $CH_3.CO.CH_2.C:C.C_6H_5$.

ACETOPHENONE ALCOHOL $C_8H_8O_2$ *i.e.* $C_6H_5.CO.CH_2OH$ v. BENZOYL-CARBINOL. An isomeric body, $C_6H_4(OH).CO.CH_3$, is described as OXY-ACETOPHENONE.

ACETOPHENONE-ANILIDE v. PHENYL-AMIDO-ACETOPHENONE.

ACETOPHENONE-BENZIL $C_{22}H_{18}O_3$ [102°]. Acetophenone and powdered benzil in equivalent proportions are shaken with an excess of conc. KOH (S. G. 1·27). After a few days a solid cake is formed, which is washed with water and then treated with ether. This leaves dehydro-acetophenone-benzil undissolved, and on evaporation deposits oblique prisms of acetophenone-benzil, which should be recrystallised from alcohol. It is v. sol. ether or hot alcohol, sl. sol. cold alcohol. Above its melting-point it gives off acetophenone. Its constitution is probably Ph.CO.CPh(OH).CH_2.CO.Ph (Japp a. Miller, *C. J.* 47, 34).

Dehydro-acetophenone benzil $C_{22}H_{16}O_2$ [129°].

Formation.—See above.

Preparation.—Equivalent quantities of acetophenone are shaken with excess of conc. KOH (S.G. 1·27) and kept liquid for some hours by the application of sufficient heat. The product is treated as described above, but ether extracts hardly anything. The residue insoluble in ether is crystallised from alcohol (J. a. M.).

$$C_{14}H_{10}O_2 + C_8H_8O = C_{22}H_{16}O_2 + H_2O.$$

Properties.—Tufts of flat needles (from alcohol). V. sl. sol. ether or cold alcohol, v. sol. boiling alcohol.

Reactions.—*Bromine* added to its solution in chloroform unites forming large reddish crystals which are apparently the tetrabromide $C_{22}H_{16}O_2Br_4$ [110°–115°]. Becomes dark at 70°, and pale again at 80°. The bromine is given off in a few weeks over lime.

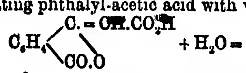
Constitution.—Dehydro-acetophenone-benzil differs from dehydro-acetone-benzil not only in forming a bromide but also in having a very much lower melting-point than would be expected if they were of analogous structure. Japp a. Miller assign to dehydro-acetone-benzil the formula $Ph.CO.CPh{<}{}^{CH_2}_{CH_2}{>}CO$, and the unsaturated formula Ph.CO.CPh:CH.CO.Ph to dehydro-acetophenone-benzil. The latter formula can, however, account only for a di- and not for a tetra-bromide (*C. J.* 47, 37).

ACETOPHENONE CARBOXYLIC ACIDS.

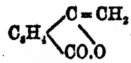
Acetophenone ω-Carboxylic Acid $C_9H_8O_3$ $C_6H_5.CO.CH_2.CO_2H$ v. BENZOYL-ACETIC ACID.

Acetophenone o-Carboxylic Acid [1 : 2] $CO_2H.C_6H_4.CO.CH_3$. *o-Acetyl-benzoic acid.* [115°].

Formation.—1. Together with CO_2, from acetophenone di-carboxylic acid by heating, long boiling with water, or by potash-fusion.—2. By heating phthalyl-acetic acid with water at 200°:



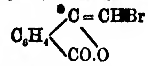
$CO_2H.C_6H_4.CO.CH_3 + CO_2$ (Gabriel a. Michael, *B.* 10, 1554).—3. From methylene-phthalide by warming with aqueous KOH (Gabriel, *B.* 17, 2524):



$+ H_2O = CO_2H.C_6H_4.CO.CH_3$.

Properties.—Broad crystals, with sweet taste.

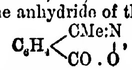
Reactions.—1. Bromine and glacial acetic acid at 100° convert it into bromo-methylene-phthalide



2. Conc. H_2SO_4 forms, in the cold, two bodies, $C_{18}H_{12}O_4$ [216°] and $C_{18}H_{14}O_5$ [c. 134°]. The latter body is a monobasic acid, di-acetophenone carboxylic acid, and splits up into CO_2 and the former body when it is heated above its melting-point (W. Roser, *B.* 17, 2620; Gabriel, *B.* 17, 2665).—3. Alcoholic NH_3 for fourteen hours at 100° forms a base, $C_{18}H_{17}N_3O_2$ [204°–210°] It crystallises in long needles, insol. water or alcohol and gives a nitroso-derivative [246°] (Gabriel, *B.* 18, 1258).—4. Ac_2O and NaOAc form $Ac.C_6H_4.CO_2Ac$ [71°]; needles, insol. alkalis (Gabriel, *B.* 14, 921).

Phenyl-hydrazide $CO_2H.C_6H_4.CMe(N_2HPh)$ [102°]. Small prisms or large tables, v. e. sol. alcohol (Roser, *B.* 18, 804).

Oxim.—The anhydride of this body,



[159°] is formed by the action of hydroxylamine (base) on acetophenone-o-carboxylic ether, or of hydroxylamine hydrochloride upon acetophenone di-carboxylic ether. It is also got, together with CO_2, when the oxim of acetophenone di-carboxylic acid is heated. It crystallises in colourless needles (Gabriel, *B.* 16, 1993).

Acetophenone p-Carboxylic Acid $C_9H_8O_3$ [1 : 4] $CO_2H.C_6H_4.CO.CH_3$. [200°]. Formed, together with terephthalic acid, by warming *exo-oxy-isopropyl-benzoic acid* $Me_2C(OH).C_6H_4.CO_2H$ with chromic mixture (R. Meyer, *B.* 12, 1071; *A.* 219, 259). The process is similar to that by which tri-methyl-carbinol is converted into acetone. Needles (from water). May be sublimed. V. sl. sol. cold water, sl. sol. hot water, alcohol or ether.

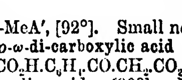
Salts.—$BaA'_2\frac{1}{2}aq$.—CuA'_2aq.—$PbA'_2 1\frac{1}{2}aq$.—AgA'.

Methyl ether.—MeA', [92°]. Small needles.

Acetophenone o-ω-di-carboxylic acid $C_{10}H_8O_5aq$ *i.e.* $CO_2H.C_6H_4.CO.CH_2.CO_2H$ aq. *Benzoyl-acet-carboxylic acid.* [90°]. Formed by dissolving phthalyl-acetic acid (*q. v.*) in cold aqueous NaOH and ppg. by HCl (Gabriel a. Michael, *B.* 10, 1553). It behaves, therefore, as if phthalyl-acetic acid were its anhydride. Broad needles (from water). On melting, it splits up into H_2O, CO_2 and acetophenone o-carboxylic acid (*q. v.*).

Salt: AgA': granular pp.

Phenyl-hydrazine, in alcoholic solution in presence of HOAc, forms the anhydride of the phenyl-hydrazide:



It is soluble in NaOHAq and is reppd. by HCl. [160°] giving off CO_2. It forms salts, *e.g.*: $(C_{16}H_{11}N_2O_3)_2Ca3aq$ (W. Roser, *B.* 18, 808).

Hydroxylamine forms, in like manner, not the *oxim* but its anhydride;

$$C_6H_4\left\langle\begin{array}{l}C - CH_2CO_2H\\ CO.O.\end{array}\right\rangle N$$

[c. 150°]. This is a mono-basic acid, and splits up, when heated, into CO_2 and the anhydride of the oxim of acetophenone-*o*-carboxylic acid (*above*).

ACETOPHENONE CHLORIDE *v.* DI-CHLORO-ETHYL-BENZENE.

ACETOPHENONE CYANHYDRIN C_9H_9NO, *i.e.* Ph.C(OH)(CN).Me *a-oxy-a-phenyl-propio-nitrile, a-oxy-hydro-atropo-nitrile.* Formed by mixing acetophenone with KCN, and adding fuming HCl (Spiegel, *B.* 14, 235). A brown oil.

Reactions.—1. KOHAq gives atrolactic acid, $Ph.CMe(OH).CO_2H$.—2. HCl at 130° gives chloro-hydro-atropic acid: $Ph.CH(CH_2Cl).CO_2H$ (Spiegel, *B.* 14, 1352).—3. *Ammonia* forms $Ph.C(NH_2)(CN).Me$ (Tiemann a. Köhler, *B.* 14, 1980).

ACETOPHENONE-DI-METHYL-ANILINE *v.* DI-METHYL-AMIDO-BENZYL PHENYL KETONE.

ACETOPHENONE DI-METHYL-HYDRAZIDE $C_{10}H_{14}N_2$, *i.e.* $PhCMe:N_2Me_2$ (165°) at 190 mm. Formed from acetophenone and di-methyl-hydrazine at 100° (Riesenegger, *B.* 16, 663).

ACETOPHENONE NITRANILIDE *v.* NITRO-PHENYL-AMIDO-ACETOPHENONE.

ACETOPHENONE PHENYL-HYDRAZIDE $C_{14}H_{14}N_2$ *i.e.* $CPhMe:N_2PhH$ [105°]. Formed by shaking acetophenone suspended in water with a solution of phenyl-hydrazine hydrochloride and sodium acetate (Fischer, *B.* 17, 576). Also by allowing a conc. alcoholic solution of phenyl-hydrazine and acetophenone to stand for a day (Riesenegger, *B.* 16, 661), or by heating the oxim with phenyl-hydrazine (Just, *B.* 19, 1206). Slender white needles or plates. V. sol. ether, sl. sol. water or cold alcohol.

ACETOPHENONE-(β)-PINACOLINE $C_{16}H_{16}O$, *i.e.* $Ph_2CMe.CO.CH_3$ (?). [41°]. (310° uncorr.). Prepared by the action of zinc and HCl on an alcoholic solution of acetophenone. Rhombic prisms or short pillars. Soluble in C_6H_6, ether, acetic acid, hot alcohol, &c. By heating with soda-lime it gives HOAc and di-phenyl-methyl-methane, $Ph_2CH.CH_3$. On reduction with HI and P, it gives a hydrocarbon $C_{16}H_{18}$ [128°], which is apparently identical with the hydrocarbon formed by the action of Na on bromo-ethyl-benzene: PhCHMe.CHMePh. CrO_3 oxidises it to di-phenyl-propionic acid, $CH_3CPh_2CO_2H$.

It An isomeric acetophenone-pinacoline [70°] in p 43° i. V.) is formed when acetophenone is base. Fu with HI and P at 140° (Graebe, *B.* 7, $C_{23}H_{14}(NO_2$ forms plates or tables (from alcohol). Acetophenin acked by AcCl; HI reduces it to the $C_{16}H_{18}$ (Thörner a. Zincke, *B.* 11.

N ONE-PINACONE

(Engler a. Riehm, $C_6H_5 - C(OH) - CH_3$ internally it reappear $H_5 - C(OH) - CH_3$ puric acid, having, dou e action of sodium oxidised as in *Reaction* 1 of acetophenone in 123, 288). prisms. V. sol.

It is split up on

Besides the derivatives desc henyl-methyl- also: AMIDO-ACETOPHENONE, BROMO-A nvert it into BROMO-NITRO-ACETOPHENONE, IODO-ACET e.CO.CH_3 DI-METHYL-AMIDO-ACETOPHENONE, NITRO PHENONE, THIO-ACETOPHENONE, ACETOPHEN-

ACETOPHEN-OXIM C_8H_9NO, *i.e.* PhCMe:NOH [59°]. *Phenyl methyl ketoxim.* Formed by mixing alcoholic solutions of acetophenone and hydroxylamine; after 24 hours, the alcohol is distilled off, and the product crystallised from water. It forms colourless silky needles. Volatile with steam; soluble in hot water, alcohol, ether, benzene, chloroform, or benzoline. Soluble in acids and in alkalis.

ACETO-PROPIONIC ACID *v.* ACETYL-PROPIONIC ACID.

ACETO-SINAPIC ACID *v.* SINAPIC ACID.

ACETO-SUCCINIC ACID *v.* ACETYL-SUCCINIC ACID.

ACETO-THIENONE *v.* THIENYL METHYL KETONE.

ACETO-THIO-TOLUIDIDE *v.* THIO-ACETYL-TOLUIDINE.

ACETO-VALERIC ACID *v.* ACETYL-VALERIC ACID.

ACETOXIM C_3H_7NO, *i.e.* $Me_2C:NOH$ *Di-methyl-ketoxim, acetone hydroxylamide* [60°] (135° i. V.) at 730 mm. Prepared by leaving an aqueous solution of acetone mixed with hydroxylamine hydrochloride, neutralised with NaOH, to stand for 24 hours; and extracting with ether (V. Meyer a. Janny, *B.* 15, 1324).

Properties.—Colourless prisms; extremely volatile and smelling like chloral. Very soluble in water, alcohol, ether, or benzoline. Neutral to litmus. Ether extracts it from a neutral, but not from an acid or alkaline, solution. It is readily decomposed by boiling acids (even acetic) into acetone and hydroxylamine. Acid reducing agents have a like effect, but zinc dust and NaOH does not affect it.

B'HCl, white powder [c. 100°], very unstable, formed by passing HCl gas into a dry ethereal solution of acetoxim.—$C_3H_6NONaOEt$, crystalline scales, got by adding NaOEt to an ethereal solution.

Benzoyl derivative $Me_2C:N(OBz)$, [42°], small colourless tables, very soluble in alcohol and ether, slightly in water; formed by the action of benzoyl chloride on acetoxim.

Benzyl ether $Me_2C:N(OC_7H_7)$, (c. 190°), oily fluid, soluble in alcohol and ether, insoluble in water; formed by the action of benzyl chloride and sodium ethylate on acetoxim; on warming with aqueous HCl, it is split up into benzyl-hydroxylamine ($H_2N.OC_7H_7$) and acetone (Janny, *B.* 16, 170).

ACETOXIMIC ACID $C_3H_6N_2O_2$, *i.e.* $CH_3.C(NOH).CH(NOH)$. *Nitroso-acetoxim, Di-nitroso-propane* [153°]. *Formation.*—(1) By the action of hydroxylamine on *u*-di-chlor-acetone ($CH_3.CO.CHCl_2$).—(2) By the action of hydroxylamine on nitroso-acetone ($CH_3.CO.CH(NOH)$) (Meyer a. Janny, *B.* 15, 1165). Small prisms. Soluble in alcohol, ether, and hot water. Its alkaline solutions are colourless.

ACETOXYL. Kolbe's name for ACETYL. Now used to denote $C_2H_3O_2$.

ACET-TOLUIDE *v.* *Acetyl*-TOLUIDINE.

ACET-TOLYL-IMID-TOLYL-AMIDE *v.* TOLYL-ACETAMIDINE.

ACETURIC ACID $C_4H_7NO_3$ *i.e.* $CH_2(NHAc).CO_2H$ (*acetyl-glycocoll, acetyl-glycine,* or *acetamido-acetic acid*). [206°]. S. (at 15°) 2·7.

***Formation*: 1. By heating glycocoll with**

Lo_2O. 2. By heating glycocoll-silver with acetyl-chloride (Kraut a. Hartmann, *A.* 138, 99).

Long colourless crystals, readily soluble in hot water and in alcohol, insoluble in ether, chloroform and benzene.

Reactions.—Gives a red coloration with Fe_2Cl_6. Readily saponified by boiling with acids or alkalis.

Salts.—$A'NH_4$ aq: soluble needles or large tables.—A'Ag: soluble plates.—A'_2Ba5aq: easily soluble needles. — $A'_2Cu4\frac{1}{2}aq$: blue trimetric prisms, easily soluble in water and in alcohol.—A'HHCl^x: needles, decomposed by water.

Methyl ether.—A'Me, [59°], (254°) at 712 mm., long colourless tables, easily soluble in water, alcohol, and benzene, sparingly in ether.

Ethyl ether.—A'Et, [48°], (260°) at 712 mm., trimetric plates.

Amide $CH_2(NHAc).CO.NH_2$—[137°], large colourless tables, soluble in water and alcohol, insoluble in ether (Curtius, *B.* 17, 1663).

ACETUREÏDE *v. Acetyl*-Urea.

ACET-XYLIDE *v. Acetyl*-Xylidine.

ACETYL C_2H_3O, $CO.CH_3$, COMe or Ac. The radicle of acetic acid, &c. The name *Acetyl* was formerly applied to the radicle C_2H_3. The prefix *acet-* often indicates the radicle $CH_3.C$; as in acetamidine; sometimes it is merely a contraction for acetyl, as in acet-xylide. The acetyl derivatives obtained by displacing H in OH or in NH_2 or in NH are described under the compounds from which they are derived by this displacement.

DI-ACETYL $C_4H_6O_2$ *i.e.* $CH_3.CO.CO.CH_3$. The oxim, $CH_3.C(NOH).C(NOH).CH_3$, of this hypothetical body, called also *di-methyl-glyoxim* or *methyl-ethyl-acetoximic acid*, is formed by adding hydroxylamine hydrochloride to an aqueous solution of methyl oximido-ethyl ketone, $CH_3.CO.C(NOH).CH_3$. Glittering needles (Schramm, *B.* 16, 180).

DI-ACETYL-ACETONE DI-CARBOXYLIC ACID *v.* Aceto-acetic ether, *Reaction* 32.

ACETYL-ACETOPHENONE *v.* Benzoyl-acetone.

ACETYL-ACRYLIC ACID *v.* Tetric acid.

DI-a_1-a_2-ACETYL-ADIPIC ACID $C_{10}H_{14}O_6$ *i.e.* $CO_2H.CHAc.CH_2.CH_2.CHAc.CO_2H$.

Di-ethyl-ether.—Et_2A''. Formed as a by-product (20 p.c.) of the action of ethylene bromide upon sodio-aceto-acetic ether, and found in the residue after distilling with steam. It is a thick colourless oil; its alcoholic solution gives a dark reddish-violet coloration with Fe_2Cl_6.

Reactions.—1. It gives a tolerably stable di-sodio-derivative which, on treatment with *iodine*, yields the di-ethylic ether of di-acetyl-tetra-methylene-di-carboxylic-acid, $\begin{array}{l}CH_2CAc.CO_2H\\ |\quad\ |\\ CH_2CAc.CO_2H\end{array}$; an acid which crystallises (with 2aq) in pearly scales [210°].—2. By conc. NH_3 di-acetyl-adipic ether is converted into the ketone-imide, $C_{14}H_{24}N_2O_4$ [177°].—3. *Phenyl-hydrazine* forms the phenyl-hydrazide [145°], which readily splits off alcohol giving ethylene-di-methyl-di-oxy-di-quinizine,

$$C_6H_4\Big\langle\begin{array}{l}N_2H:CMe\qquad\qquad\quad Me.C:HN_2\\ \qquad\quad\ |\qquad\qquad\qquad\quad\ |\\ CO\ .\ CH.CH_2.CH_2.CH.CO\end{array}\Big\rangle C_6H_4$$

4. By *distillation*, or on solution in conc. H_2SO_4, it loses H_2O, giving an ether $C_{14}H_{20}O_5$ which probably has the constitution

$$CH\Big\langle\!\!\langle\begin{array}{l}CMe.CH(CO_2Et).CH_2\\ CO\ .\ CH(CO_2Et).CH_2\end{array}\Big\rangle$$

The corresponding acid, [189°], forms a phenyl-hydrazide, $C_{10}H_{12}O_4(N_2PhH)$ [192°] (Perkin a. Obrembsky, *B.* 19, 2051).

ACETYL-AMIDO COMPOUNDS *v.* Amido compounds.

ACETYL-BENZOIC ACID *v.* Acetophenone carboxylic acid.

ACETYL-BENZOYL-ETHANE *v.* Acetophenone-acetone.

ACETYL-BENZOYL-ETHANE CARBOXYLIC ACID *v.* Acetophenone-aceto-acetic acid.

ACETYL-BENZYL-SUCCINIC ETHER $C_{17}H_{22}O_5$ *i.e.* $CO_2Et.CAc(CH_2Ph).CH_2.CO_2Et$ (310°) S.G. $\frac{15}{15}$ 1·088. Prepared by the action of benzyl chloride on a mixture of sodium ethylate and acetyl-succinic ether (Conrad, *B.* 11, 1058).

ACETYL BROMIDE C_2H_3OBr *i.e.* $CH_3.CO.Br$. *Acetic bromide* (81°). Formed by treating acetic acid with PBr_5 (Ritter, *A.* 95, 209). Prepared by gradually adding 240 g. bromine to a mixture of 90 g. glacial acetic acid and 33 g. amorphous phosphorus, and distilling when the action is complete (Gal, *A.* 129, 537). Hanriot (*A. Ch.* [5] 17, 83) uses 1 pt. phosphorus, 15 acetic acid and 40 bromine. Colourless fuming liquid. Heated with bromine at 100° in a sealed tube, it yields bromacetyl-bromide $C_2H_2BrO.Br$, together with more highly brominated compounds, which may be separated by fractional distillation (Gal). On the action of bromine on C_2H_3OBr, see also Urech (*B.* 13, 1720; *J.* 1880, 386). H. W.

ACETYL-BUTANE-PHOSPHONIC ACID *v.* Di-acetone-phosphinic acid.

ACETYL-BUTYL ALCOHOL $C_6H_{12}O_2$.

Di-acetonic alcohol $CH_3.CO.CH_2.CMe_2.OH$. (164°). S.G. $\frac{25}{}$ ·931.

Preparation.—Acid oxalate of di-acetonamine (1 pt.) is dissolved in water (3 pts.) and cooled to 5°, when it deposits some of the salt; solid KNO_2 (2 pts.) is slowly added, and the mixture kept cool for some days and then heated to 50° or 60°; the oily layer (mesityl oxide) is removed partly by distillation, partly by a tap-funnel; and the aqueous solution, neutralised with K_2CO_3, is shaken with ether (Heintz, *A.* 169, 114; 178, 342).

Properties.—Syrup, miscible with water, alcohol, or ether, gives off hydrogen when treated with Na.

γ-Acetyl-*n*-butyl Alcohol $C_6H_{12}O_2$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH_2OH$. *Methyl δ-oxy-n-butyl ketone.* (155°) at 718 mm. S.G. $\frac{0}{}$ 1·0143.

Formation.— 1. From bromo-propyl-aceto-acetic ether (50 g.) by boiling for an hour with water (50 g.) and HCl (20 g. of S.G. 1·18) (Lipp, *B.* 18, 3280).—2. From so-called tetra-methylene methyl ketone carboxylic acid by boiling with water (Perkin, jun., *B.* 19, 2557).

Properties.—Liquid with camphor-like smell, v. sol. water, alcohol, and ether; scarcely volatile with steam. It does not reduce Fehling's solution or ammoniacal $AgNO_3$. *Chromic mixture* oxidises it to δ-acetyl-*n*-butyric acid. *Sodium amalgam* reduces it to ω-δ-di-oxy-hexane.

Anhydride $C_6H_{10}O$ *i.e.* $CH_2\Big\langle\begin{array}{l}CH:CMe\\ CH_2.CH_2\end{array}\Big\rangle O$.

Oil. Formed by distilling the alcohol or the following acid.

Tetra-methylene methyl ketone carboxylic acid, $C_7H_{10}O_3$, appears to be a carboxylic acid formed from the anhydride of acetyl-butyl alcohol: $CH_2<\begin{matrix}C(CO_2H):CMe\\CH_2\ .\ CH_2\end{matrix}>O$.

Its ethyl ether $C_9H_{14}O_3$, (223°), M.M. 10·195, is formed by the action of trimethylene bromide on aceto-acetic ether (v. p. 24).

ACETYL-BUTYL BROMIDE $C_6H_{11}BrO$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH_2.Br$. (215°) at 718 mm. From the preceding acid, $C_7H_{10}O_3$, or from acetyl-butyl alcohol by the action of HBr. Also formed by heating bromo-propyl-aceto-acetic ether with dilute acids. It is a colourless oil, v. sol. alcohol or ether, v. sl. sol. water; boiling water converts it into the alcohol (Lipp, *B.* 18, 3281; Perkin, *B.* 19, 2557).

ACETYL-BUTYRIC ACIDS $C_6H_{10}O_3$.

α-Acetyl-*n*-butyric acid $CH_3.CH_2.CHAc.CO_2H$ *v. Ethyl-aceto-acetic acid* under ACETO-ACETIC ACID.

β-Acetyl-*n*-butyric acid $CH_3.CHAc.CH_2.CO_2H$. [c.-12°]. (242°). Formed, together with its ether, by boiling α-acetyl-α-methyl-succinic ether, $CO_2Et.CMeAc.CH_2.CO_2Et$, with HCl (Bischoff, *A.* 206, 331).

Very hygroscopic liquid. V. sol. water, alcohol, or ether. Oxidises in air. Hot dilute HNO_3 forms pyrotartaric acid.

Salts. — ZnA'_2 (at 100°): nodules (from alcohol). The salts of the alkalis and alkaline earths are syrupy, the lead salt may be got as a vitreous mass.

Ether.—EtA' (204° 205°). Oil.

γ-Acetyl-*n*-butyric acid $CH_2Ac.CH_2.CH_2.CO_2H$ [13°]. (c. 275° i. V.). From sodium aceto-acetic ether and β-iodopropionic ether (Fittig a. Wolff, *A.* 216, 127). Thick liquid. V. sol. water, alcohol, or ether. Solutions are acid and decompose Na_2CO_3. Forms a crystalline compound with water, $CH_3.C(OH)_2.CH_2.CH_2.CH_2.CO_2H$ [35°-36°] which forms monoclinic prisms,

$a:b:c = \cdot769:1:\cdot885\ \ \beta = 75°\ 20'$.

Over H_2SO_4 it loses H_2O, becoming liquid.

Salts. — $Ca(C_6H_9O_3)_2aq.$ — $Pb(C_6H_9O_3)_2aq.$ — ZnA'_2.—AgA'.

Reactions.—Sodium amalgam reduces it to δ-OXY-HEXOIC ACID (*q. v.*).

α-Acetyl-iso-butyric acid $(CH_3)_2CAc.CO_2H$ *v. di-methyl-aceto-acetic acid* under ACETO-ACETIC ACID.

β-Acetyl-iso-butyric acid $CH_2Ac.CMeH.CO_2H$ (248°). Formed, together with its ether and CO_2, by boiling α-acetyl-β-methyl-succinic ether, $CO_2Et.CHAc.CHMe.CO_2Et$, with HCl (Bischoff, *A.* 206, 319). It is a liquid. V. sol. water, alcohol, or ether. Turns brown in air. Dilute HNO_3 forms pyrotartaric acid. The salts are amorphous. The silver salt deposits silver on warming its solution.

Ether.—EtA' (206°-208°). Oil.

ACETYL-TRI-CARBALLYLIC ETHER $C_{14}H_{22}O_7$, *i.e.* $CO_2Et.CH_2.CAc(CO_2Et).CH_2.CO_2Et$. From chloro-acetic ether and sodium acetyl-succinic ether, $CO_2Et.CH_2.CAcNa.CO_2Et$ (Miehle, *A.* 190, 323). It boils with much decomposition at 280°-300°. Boiling baryta water or conc. alcoholic KOH split it up completely into alcohol, acetic, and tri-carballylic, acids.

ACETYL-CARBINOL $C_3H_6O_2$ *i.e.* $CH_3.CO.CH_2OH$. *Pyruvyl alcohol, Oxy-acetone, Acetol.*

Formation.—Conc. H_2SO_4 dissolves β-chloro allyl alcohol, $CH_2:CCl.CH_2OH$, giving off HCl the solution is diluted and distilled (Henry *Bl.* 39, 526).

Ethyl ether.—$CH_3.CO.CH_2.OEt$. (128°) S.G. $\frac{18}{}$ ·92. Formed by heating propargyl ether $CH:C.CH_2OEt$, with water and $HgBr_2$ (Henry *C. R.* 93, 421). Colourless liquid with peculiar odour and burning taste.

Acetyl derivative $C_3H_5O(OAc)$. Colourless fluid. (172°) S.G. $\frac{11}{}$ 1·053. Soluble in water. Prepared by heating potassium acetate with chloracetone. Also from propargyl acetate, water, and $HgBr_2$. The alcohol has not been got by its saponification. Readily reduces ammoniacal silver nitrate or Fehling's solution, the chief product of the oxidation being lactic acid.

Benzoyl derivative $C_3H_5O(OBz)$. Long needles. [24°]. Soluble in hot water, easily in alcohol and ether. Prepared by heating potassium benzoate with chloracetone. (Breuer a. Zincke, *B.* 13, 637.)

ACETYL CHLORIDE $C_2H_3O.Cl$, *i.e.* Ac.Cl. *Acetic chloride.* M.w. 78·5. (50·9° cor.) (Thorpe, *C. J.* 37, 188); (51°-52°) at 720 mm. (Brühl, *A.* 203, 14). S. G. $\frac{0}{4}$ 1·1377 (T.); $\frac{20}{4}$ 1·1051. C. E. (0°-10°) ·001391; (0°-50°) ·001504 S. V. 74·05 (T.). μ_β 1·3954. R_∞ 26·82 (B.). H.F.p. 63,300 (Berthelot).

Formation.—1. From $POCl_3$ and potassic acetate: $3KOAc + POCl_3 = K_3PO_4 + 3AcCl$ (Gerhardt, *A. Ch.* [3] 37, 294).—2. Contained in the more volatile portions of the product of the action of chlorine on aldehyde (Wurtz, *A. Ch.* [3] 49, 58). 3. By distilling glacial acetic acid with PCl_5: $HOAc + PCl_5 = AcCl + ClH + POCl_3$ (Ritter, *A.* 95, 209).

Preparation.—By distilling glacial acetic acid (61g.) with phosphorus trichloride (93g.) (Béchamp, *J.* 1856, 427). The reaction is as follows (Thorpe, *C. J.* 37, 186):

$$3HOAc + 2PCl_3 = 3AcCl + 3HCl + P_2O_3.$$

If more HOAc be used Ac_2O is also formed. The action of PCl_3 is therefore precisely like that of PCl_5, amounting to a displacement of O by Cl_2; the molecule HCl_2Ac, which might be expected to be formed, cannot hold together on account of the monovalent character of chlorine, and so splits up at once into HCl and ClAc. Under precisely similar conditions, alcohol, HOEt, gives HCl and ClEt.

Properties.—Colourless, fuming, mobile, and strongly refracting liquid. Its vapour strongly attacks the eyes and respiratory organs.

Reactions.—1. Violently acted on by *water*, with formation of HCl and acetic acid.—2. With *ammonia* it yields acetamide $AcCl + NH_3 = HCl + AcNH_2$ and with *aniline* in like manner, acetanilide, AcNHPh.—3. Distilled with *potassium acetate* or *benzoate*, it forms acetic or aceto-benzoic oxide: $KOAc + AcCl = KCl + Ac_2O$; and $KOBz + AcCl = KCl + AcOBz$. Similarly with salts of other acids.—4. With *potassium hydrosulphide* it yields acetic hydrosulphide or thioacetic acid, and with *potassium monosulphide* it forms acetic sulphide or thioacetic anhydride, $AcCl + KSH = KCl + AcSH$; and $2AcCl + K_2S = 2KCl + Ac_2S$ (Jacquemin a. Vosselmann, *C. R.* 49, 371).—5. With *potassium nitrite* it gives off nitrosyl-chloride, and towards the end of the reaction NO_2, and on heating the residue to 150°,

acetic anhydride distils over: $AcCl + KNO_2 = NOCl + KOAc$, and $AcCl + KOAc = KCl + Ac_2O$ (Armstrong, *C. J.* 26, 683).—6. *Silver nitrate* acts: $2AcCl + AgNO_3 = AgCl + NO_2 + Cl + Ac_2O$. Similarly with other nitrates: $Hg(NO_3)_2$, $Pb(NO_3)_2$, and KNO_3 are attacked immediately; $Ba(NO_3)_2$ is not affected; $Cu(NO_3)_2$ readily. With KNO_3, chlorine is first evolved, NO_2 only towards the end (Armstrong).—7. With *succinic acid* it yields acetic acid and succinic anhydride,

$$C_2H_4(COOH)_2 + CH_3.CO.Cl = HCl + CH_3.COOH + C_2H_4(CO)_2O;$$

and it reacts in like manner with other dibasic dihydric acids; viz., isodibromosuccinic, phthalic, diphonic, and camphoric acids; isosuccinic, ordinary dibromosuccinic, fumaric, and terephthalic acids are not attacked; sublimed anhydrous oxalic acid is resolved into H_2O,CO, and CO_2; benzoic acid yields benzoic chloride and acetic acid (Anschütz, *B.* 10, 325, 1881).—8. With *titanic chloride*, acetyl chloride forms the compound $TiCl_4AcCl$ (Bertrand, *Bl.* [2] 33, 403). Large transparent octahedral crystals [25°-30°] sol. in CS_2.—9. *Aluminium chloride* reacts according to the equation $Al_2Cl_6 + 4(CH_3.CO)Cl = 4HCl + 2(CH_3.CO.CH:CO),Al_2Cl_6$ (Winogradoff, *Bl.* [2] 34, 325). The product is a solid, decomposed by water into CO_2 and acetone.—10. PCl_5 at 190° forms chloro-acetyl chloride $CH_2Cl.CO.Cl$ (Samosadsky, *Z.* 1870, 105), and trichloro-acetyl chloride, $CCl_3.CO.Cl$ (Hübner, *A.* 120, 330).—11. *Zinc* produces a brown mass whence alcohol extracts '**acetylide**,' $C_{16}H_{18}O_4$, which may be ppd. by water. Red plates (from chloroform). Sol. ether, alcohol, HClAq, fuming HNO_3, or Ac_2O. Combines with bromine; does not reduce Fehling's solution (Tommasi a. Quesneville, *C. R.* 76, 496).—12. Acts upon *benzene*, in presence of $AlCl_3$, with formation of acetophenone (*q. v.*).—13. Acts similarly upon *thiophene*, or its mono-haloid derivatives, displacing, in presence of $AlCl_3$, H by Ac. But in di-bromo- or di-iodo-thiophene it displaces, in presence of $AlCl_3$, Br or I by Ac, *e.g.*:

$$C_4H_2SBr_2 + ClAc = C_4H_2SBrAc + ClBr$$

(Gattermann a. Römer, *B.* 19, 688). H. W.

Use in Organic Investigations.—Acetyl chloride evolves HCl when it is heated with any substance containing the radicles hydroxyl, amidogen, or imidogen. Hence, if a substance does not evolve HCl when so treated, it may be assumed to be free from these radicles. If the hydroxyl be alcoholic, *i.e.* attached to an atom of carbon that is not attached to any more oxygen, it will be converted into acetoxyl (AcO); and, if the substance contains no nitrogen, the number of acetoxyls it contains after this treatment gives the number of alcoholic hydroxyls the body contains. Before making the experiment, all carboxyls should be etherified, since the group CO_2H is attacked by AcCl (*v. Reaction* 7), while the group CO_2Et is not attacked. The number of acetyl groups that have entered may in many cases be determined by boiling with standard alkali and subsequent titration (Schiff). Acetyl chloride converts NH_2 into NHAc, but hardly ever into NAc_2. It converts NH into NAc. It has no action upon tertiary amines, hence it can be used in the diagnosis of bases. Acetyl chloride does not act upon hydrogen directly united to carbon, except in presence of $AlCl_3$ or some similar agent.

ACETYL CYANIDE C_3H_3ON or AcCN *Pyruvo-nitrile.* M. w. 69. (93°). V.D. 2·4.

Preparation.—When acetyl chloride and silver cyanide are heated together in a sealed tube at 100°, and the product is distilled, a colourless liquid passes over at 80°-90°, and afterwards a compound having a much higher boiling-point. The first yields acetyl cyanide on rectification.

Properties.—Oil, lighter than water, which gradually dissolves it, forming HCN and HOAc, converted by HCl first into $CH_3.CO.CONH_2$, and subsequently into pyruvic acid (Hübner, *A.* 120, 330; 123, 271; see also Fileti, *G.* 5, 391; *J.* 1875, 510).

Di-acetyl-di-cyanide $C_6H_6O_2N_2$ [69°] (210° cor.). V.D. 4·57 (for 4·77). Formed from acetyl cyanide by heating it with KOH, or even by keeping it for some time in a closed vessel.

Preparation.—Powdered KCN (32 pts.) is boiled with acetic anhydride (50 pts.), diluted with benzene (200 pts.): yield is 25 p.c. of the theoretical (Kleeman, *B.* 18, 256). Glistening tables, sl. sol. hot water, v. sol. alcohol, ether, or benzene. Di-acetyl-di-cyanide, like acetyl cyanide, is converted by boiling with water, H_2SO_4, or KOH, into HCN and AcOH. Heated with $AgNO_3$ it yields AgCN.

ACETYLENE C_2H_2 or CH:CH *Ethine, Ethinene.* M.w. 26. *Physical Properties of liquid acetylene*: S.G. $\frac{0}{}$ ·451; $\frac{16}{}$ ·420; $\frac{24}{}$ ·381. C.E. (-7° to 36°) ·00489. *Vapour-pressure*: 16,340 mm. at 0°; 24,900 mm. at 13·5°. *Critical Point* 37° (G. Ansdell, *Pr.* 29, 209). *Properties of gaseous acetylene*: V.D. ·91. S. 1 at 18°; S. (CS_2 or isopentane) 1; S. (CCl_4 or turpentine oil) 2; S. (amyl alcohol) 3½; S. (benzene) 4; S. (glacial acetic acid or abs. alcohol) 6 (Berthelot, *A. Ch.* [4] 9, 425). H.F.p. −47,770. H.F.v. −47,770 (*Th.*); −64,000 (Berthelot).

Occurrence.—In coal-gas (Boettger, *A.* 109, 351).

Formation.—1. Synthetically by passing hydrogen gas over charcoal heated to whiteness in the electric arc (Berthelot, *C. R.* 54, 640); the hydrogen may be passed through holes drilled through the centre of carbon points discharging powerful sparks (Dewar, *Pr.* 29, 188).—2. By exposing marsh-gas or coal-gas to a strong heat, or to the spark of a powerful induction-coil: $2CH_4 = C_2H_2 + 3H_2$ (Berthelot, *C. R.* 54, 515). Part of the C_2H_2 is, however, polymerised during the process, being converted partly into benzene C_6H_6, partly into black tarry hydrocarbons (Berthelot, *Bl.* [2] 11, 142). The vapours of many other organic compounds, as ethylene, alcohol, ether, acetone, amyl alcohol, and benzene, likewise yield acetylene when induction sparks are passed through them (De Wilde, *Bl.* [2] 6, 267).—3. By the incomplete combustion of hydrocarbons and other organic bodies—abundantly, for example, in a Bunsen lamp, when the flame strikes down and burns within the chimney—also in the incomplete oxidation of organic compounds at ordinary temperatures, as in the voltaic circuit, *e.g.* in the electrolysis of a solution of potassium aconitate or succinate (Berthelot, *Bl.* [2] 9, 103).—4. By the incomplete combustion of mixtures of hydrogen and gaseous or vaporous carbon-com-

pounds not containing hydrogen, *e.g.* CO, CS_2, CN.—5. By passing a mixture of methane and carbon monoxide through a red-hot tube: $CH_4 + CO = H_2O + C_2H_2$.—6. Together with H, CH_4, and free carbon, by passing the vapour of methyl chloride (Berthelot), or of ethylene chloride (De Wilde), or of pentane from American petroleum (Vohl, *Bl.* 4, 302), through a red-hot tube.—7. Together with benzene, by passing styrene vapour through a red-hot tube: $C_8H_8 = C_2H_2 + C_6H_6$ (Berthelot, *J.* 1866, 511).—8. By passing chloroform vapour over red-hot copper: $2CHCl_3 + Cu_6 = 3Cu_2Cl_2 + C_2H_2$ (Berthelot), or by treating chloroform with potassium-amalgam (Kletzinsky, *Z.* 1866, 127), or with sodium (Fittig, *ibid.*). — 9. From iodoform by the action of finely divided silver either alone or mixed with finely divided copper: $2CHI_3 + 3Ag_2 = 6AgI + C_2H_2$. Also by the action of finely divided zinc or of the zinc-copper couple on iodoform in presence of water (P. Cazeneuve, *C. R.* 97, 1371; *Bl.* [2] 41, 156).—10. By passing a mixture of CO and HCl over red-hot magnesium silicide (Berthelot). — 11. By the action of alcoholic potash on bromethylene: $C_2H_3Br + KOH = KBr + H_2O + C_2H_2$ (Sawitsch, *C. R.* 52, 157).—12. By the action of water on calcium carbide (produced by strongly heating an alloy of Zn and Ca with charcoal): $CaC_2 + H_2O = CaO + C_2H_2$ (Wöhler, *A.* 124, 220). 13. Formed, together with succinic acid, by the electrolysis of sodium fumarate or maleate: $C_4H_2Na_2O_4 + H_2O = C_2H_2 + 2CO_2 + Na_2O + H_2$ (Kekulé, *J.* 1864, 389).—14. By heating isethionic acid with potash: $C_2H_4O.SO_3K + KOH = C_2H_2 + K_2SO_4 + 2H_2O$.—15. Formed in small quantity by heating cupric acetate (1 pt.) with water (200 pts.) in a closed flask at 100° (Tommasi, *Bl.* [2] 38, 257).

Preparation.—1. Air is burned in a cylinder full of coal-gas, and a portion of the products of combustion are sucked (by an air-pump) first through a metallic condenser to cool them, and then through several bottles containing an ammoniacal solution of cuprous chloride. A red pp., C_2Cu_2aq, is formed; this is collected, washed by decantation, and warmed with aqueous HCl, when it is decomposed with evolution of acetylene gas: $C_2Cu_2H_2O + 2HCl = C_2H_2 + 2CuCl + H_2O$ (Jungfleisch, *C. R.* 90, 264; *J. Ph.* [5] 1, 307).—2. Ethylene bromide is slowly dropped into a strong alcoholic solution of potash at boiling heat, and the evolved gas is passed through a second similar boiling solution to remove bromethylene (Miasnikoff, *A.* 118, 330; Sawitsch, *A.* 119, 184; Sabanejeff, *A.* 178, 111). To remove the last traces of bromethylene, Zeisel (*A.* 191, 372) recommends passing the gas over moderately heated soda-lime. The gas may also be purified, as in the first method, by passing it through an ammoniacal solution of cuprous chloride.

Properties.—Colourless gas, having a disagreeable odour. According to Zeisel, when prepared from the copper compound as described above, it is contaminated with vinyl chloride. Acetylene is liquefied by a pressure of 83 atmospheres at 18°, forming a mobile, highly refractive liquid, lighter than water. Liquid acetylene dissolves paraffins and many fats (Cailletet, *C. R.* 85, 851).

Reactions.—1. Decomposed by the *induction-spark* with separation of carbon, and partly converted into a liquid and a solid polyacetylene, the latter insoluble in the ordinary solvents.—2. Slowly passed through a porcelain tube *heated to bright redness* it is almost wholly resolved into C and H, together with small quantities of ethylene and of tar containing naphthalene. Acetylene is also resolved into C and H by exploding a percussion-cap in it (Berthelot, *C. R.* 93, 613). Heated to dull redness in a bent glass tube standing over mercury it is gradually polymerised, forming: a very volatile liquid probably C_4H_4, benzene C_6H_6, styrene C_8H_8 (135°-160°), a liquid mixture (210°-250°) of naphthalene $C_{10}H_8$ and probably naphthalene hydride $C_{10}H_{10}$, a mixture of strongly fluorescent oils distilling at 250°-340°, retene distilling at 360° (Berthelot, *C. R.* 62, 905).—3. Mixed with excess of *hydrogen* over mercury, and in contact with platinum-black, acetylene is converted into ethane: $C_2H_2 + 2H_2 = C_2H_6$; by alkaline reducing agents, into ethylene, C_2H_4, *e.g.* by the action of zinc and aqueous ammonia on its copper compound (Berthelot).—4. With *oxidising agents.* Converted by $KMnO_4$ into oxalic acid, $C_2H_2O_4$, with formic and carbonic acids as secondary products (Berthelot, *C. R.* 74, 35).—5. Slowly absorbed by an ammoniacal *cupric solution*, and for the most part oxidised, a carbonaceous substance being at the same time deposited, together with a small quantity of the compound $C_2Cu_2H_2O$ (Berthelot, *A. Ch.* [4] 9, 422).—6. Passed with *phosgene*, $COCl_2$, through a red-hot tube, it is polymerised to benzene (Berthelot, *Bl.* [2] 13, 9).—7. With *chlorine*, either pure or mixed with other gases, acetylene sometimes detonates, yielding HCl and free carbon. Frequently, however, $C_2H_2Cl_2$ is formed with explosion; or this compound is formed at first, and then the mixture suddenly explodes (Berthelot, *Bl.* [2] 5, 191).—8. Acetylene passed into bromine under water forms $C_2H_2Br_4$ (*v. tetra*-BROMO-ETHANE) and a non-volatile solid, a polymeride of C_2HBr_3.—9. Acetylene passed over *iodine* moistened with alcohol forms $C_2H_2I_2$ (Sabanejeff, *A.* 178, 109, *v. di*-IODO-ETHYLENE).—10. Acetylene passed into a solution of ICl in HCl forms C_2H_2ICl (Plimpton, *C. J.* 41, 392, *v.* CHLORO-IODO-ETHYLENE).—11. With *nitrogen.* When a series of strong induction-sparks is passed through a mixture of acetylene and nitrogen, hydrocyanic acid is formed, $C_2H_2 + N_2 = 2HCN$. Carbon and hydrogen are at the same time separated, but this may be prevented by diluting the gaseous mixture with 10 vol. H (Berthelot, *C. R.* 77, 1011).—12. Passed with vapour of *hydrocyanic acid* through a red-hot tube acetylene yields a small quantity of picoline C_6H_7N, and probably homologues thereof (Ramsay, *Ph. M.* [5] 4, 241). 13. Strongly heated with *butylene* and *amylene* it forms $C_2H(C_4H_9)$ and $C_2H(C_5H_{11})$ (Prunier, *A. Ch.* [5], 17, 5).—14. Successive treatment with H_2SO_4 and water forms some stable sulphonic acid (Zeisel, *A.* 191, 366).—15. Converted into aldehyde by an aqueous solution of *mercuric bromide*, even in the cold (Kutscheroff, *B.* 14, 1540):

$$CH{:}CH + H_2O = CH_2{:}CH.OH = CH_3.CHO.$$

16. $SbCl_5$ absorbs acetylene forming $C_2H_2SbCl_5$, which, on heating, splits up into $SbCl_3$ and $C_2H_2Cl_2$.—17. Conc. HBrAq at 100° forms a little bromo-ethylene (vinyl bromide).—18. Conc. HIAq

forms some iodo-ethylene and ethylidene iodide. 19. Passed through boiling *sulphur*, it forms some thiophene (V. Meyer, *B.* 16, 2176).

METALLIC DERIVATIVES.—*Sodium acetylene* C_2HNa, is formed, with evolution of hydrogen and small quantities of ethylene and ethane, when sodium is gently heated in acetylene. At a dull red heat disodium-acetylene C_2Na_2 is formed. —*Potassium* decomposes acetylene in like manner, but with greater violence; when melted in the gas it takes fire and is converted into C_2K_2, which is also formed when K is heated to dull redness on ethylene-gas. All these compounds are decomposed by water with explosive violence and reproduction of acetylene (Berthelot, *A.* 139, 150).

Calcium-acetylene C_2Ca is formed by strongly heating an alloy of zinc and calcium with charcoal. Decomposed by water into $Ca(OH)_2$ and acetylene (Wöhler, *A.* 124, 220).

Copper-acetylene $C_2Cu_2H_2O$. It may be looked upon as C_2Cu_2aq or as HC:C.Cu.Cu.OH; in the latter case it may be called *cuproso-vinyl hydroxide.* Berthelot (*A.* 138, 315) considers it to be *cuproso-vinyl oxide* $(C_2HCu_2)_2O$. It constitutes the red precipitate formed on passing acetylene or coal-gas into an ammoniacal solution of cuprous chloride. In the dry state it explodes when struck or when heated to 100°–120°, leaving a velvety black powder containing copper and charcoal. Takes fire in contact with chlorine, bromine, or finely divided iodine. Its formation affords a very delicate test for acetylene, the presence of 0·005 mg. of that compound being thus recognisable. The formula above given for it is due to Blochmann (*A.* 173, 174). According to Berthelot (*Bl.* [2] 5, 191) when acetylene is passed into a conc. solution of cuprous chloride in KCl a yellow crystalline pp. of *cuproso-vinyl chloride* C_2HCu_2Cl is formed, corresponding bromides and iodides being formed in a similar way.

Silver acetylene $C_2Ag_2H_2O$, is formed on passing acetylene into an ammoniacal solution of silver nitrate, as a white or yellowish precipitate which, when dry, explodes even more easily than the copper-compound. The above formula, due to Blochmann, is that of *argento-vinyl hydroxide*, CH:C.Ag.Ag.OH; Berthelot on the other hand regards the compound as the corresponding oxide $(C_2HAg_2)O$. The formulæ of Blochmann and Berthelot require 83·7 and 86·7 p.c. Ag respectively; Miasnikoff (A. 118, 332) finds 88 p.c. Ag in the pp., a result that has been confirmed by Plimpton, and agrees with the formula $C_2H_2 2Ag_2O$. Acetylene completely pps. the silver even from a neutral solution of $AgNO_3$; the pp. contains variable quantities of $AgNO_3$ (Plimpton). The *chloride* CH:C.Ag.Ag.Cl, is prepared by passing acetylene into an ammoniacal solution of silver chloride (Berthelot). By agitating silver acetylene with a solution of iodine in ether, till the colour of the liquid disappears and then evaporating, yellow offensive-smelling crystals are formed, the vapour of which strongly attacks the eyes (Berend, *A.* 135, 257); Baeyer (*B.* 18, 2275) has shown that they are di-iodo-acetylene: $C_2Ag_2 + 2I_2 = C_2I_2 + 2AgI$.

Gold and Mercury Compounds.—In an ammoniacal solution of aurous thiosulphate, acetylene forms a yellow highly explosive precipitate, and in an alkaline solution of potassio-mercuric iodide a yellow pp.: C_2HHgI,H_2O, which explodes slightly when heated and yields acetylene when treated with acids (Bassett, *C. N.*, 19, 28). H. W.

Theoretical considerations.—The explosive character of acetylene is undoubtedly connected with the fact that its formation from C and H is attended with disappearance of heat (Berthelot). It has been suggested by Baeyer (*B.* 18, 2277) that this disappearance of heat may be due to the production of a strained condition owing to the alteration in the direction of the attraction between the two carbon atoms.

To represent his views in a mechanical model, he supposes four steel wires fixed to a ball and radiating from it in the direction of the angles of an inscribed tetrahedron. Such a ball represents a free atom of carbon; union of such atoms is represented by a wire of one ball being attached to, and in a straight line with, a wire of another ball. If two such balls be taken and three of the wires from one ball be fastened to three of the wires from another ball and then bent in such a way that all six wires are parallel, then the arrangement is in a strained condition, for the wires will readily fly apart, representing the explosion of acetylene. The angle between two adjacent wires in one of the balls just described is 109° 28′, which is very near the angle of a pentagon (108°); hence if five balls be placed at the angles of a pentagon, very little bending will be required to make a wire from each ball in a straight line with a wire from the next. The angles of a hexagon, of a square, and of an equilateral triangle, differ by $10\frac{1}{2}°$, $19\frac{1}{2}°$, and $19\frac{1}{2}°$ respectively from $109\frac{1}{2}°$; these numbers ought therefore to indicate the relative stability of rings containing 6, 4, and 3 carbon atoms. As a matter of fact, closed rings of carbon atoms usually contain five or six atoms, while rings containing three, four, or seven atoms are almost unknown.

Haloid derivatives of acetylene *v.* BROMO-, CHLORO-, and IODO-, ACETYLENE, -ETHYLENE, and -ETHANE.

DIACETYLENE HC:C.C:CH. Gas of peculiar smell resembling dipropargyl. Formed by heating diacetylene-di-carboxylic acid with ammoniacal Cu_2Cl_2 solution. With ammoniacal Cu_2Cl_2 it gives a violet-red pp., with ammoniacal $AgNO_3$ a very explosive yellow pp. By the action of a solution of iodine upon the silver-compound di-iodo-di-acetylene is formed. (Baeyer, *B.* 18, 2272.)

ACETYLENE DI-BROMIDE *v.* DI-BROMO-ETHYLENE.

ACETYLENE TETRA-BROMIDE *v.* TETRA-BROMO-ETHANE.

ACETYLENE DI-BROMIDE DI-CARBOXYLIC ACID *v.* DI-BROMO-FUMARIC ACID.

ACETYLENE BROMO-IODIDE *v.* BROMO-IODO-ETHYLENE.

ACETYLENE CARBOXYLIC ACIDS

CH:C.CO_2H.

Acetylene mono-carboxylic acid *v.* PROPIOLIC ACID.

Acetylene-di-carboxylic acid:

$C_4H_2O_4$, *i.e.* $CO_2H.C$:$C.CO_2H$.

Formed by treating di-bromo- or iso-di-bromo-succinic acid with alcoholic KOH (4 mols.) at

100° (Bandrowski, *B.* 10, 838). The yield is 75 per cent. of the theoretical (Baeyer, *B.* 18, 677).

Separates from water in efflorescent crystals, these contain aq., which they lose over H_2SO_4, and then crystallise from ether in thick four-sided tables. The hydrated acid is v. e. sol. water, alcohol or ether, but the dry acid is less soluble. The acid decomposes when melted.

Salts.—$Na_2C_4O_4$ $3\frac{1}{2}$aq.: slender needles. — KHC_4O_4: small crystals, sl. sol. water.— $ZnC_4O_4 1\frac{1}{2}$aq. — PbC_4O_4aq. — $CuC_4O_4 3$aq.: blue plates, sl. sol. cold water (Bandrowski, *B.* 12, 2212).

Reactions.—1. The acid and its acid salts are converted, by *heating with water*, into propiolic acid: $CO_2H.C{:}C.CO_2H = CO_2H.C{:}CH + CO_2$. —2. *Sodium-amalgam* reduces it to succinic acid.—3. *Bromine* combines forming di-bromo-fumaric acid.—4. HCl, HBr, or HI combine readily forming chloro-, bromo-, or iodo-, fumaric acids.

Methyl ether Me_2A''. (197°). Colourless liquid (Bandrowski, *B.* 15, 2694).

Acetylene tetra-carboxylic acid, so called, *v.* ETHANE TETRA-CARBOXYLIC ACID.

Di-acetylene di-carboxylic acid $C_6H_2O_4$aq. *i.e.* $CO_2H.C{:}C.C{:}C.CO_2H$ aq. Prepared by the action of a concentrated aqueous solution of potassic ferricyanide upon a cooled magma of the cuprous compound of sodium propiolate:

$$2CuC{:}C.CO_2Na + O_2 = 2CuO + (C{:}C.CO_2Na)_2.$$

Colourle[illegible] O_2 + H_2O = [illegible] 121. 220. 18 [illegible] needles or tables, v. sol. water, alcohol, or ether, v. sl. sol. benzene or benzoline. Turns brown at 100° and explodes very violently at c. 177°. Explodes also on percussion. Turned purple by light. Gives a brownish-red pp. with ammoniacal cuprous chloride.

Reactions.—1. *Sodium-amalgam* reduces it to hydro-muconic acid,

$$CO_2H.CH{:}CH.CH_2.CH_2.CO_2H,$$

and adipic acid, $CO_2H.CH_2.CH_2.CH_2.CH_2.CO_2H$; some propionic is formed at the same time.—2. *Zinc dust* and HCl also reduce it to adipic acid.

Ether.—Et_2A'' (184°) at 200 mm. An oil. Reduced by zinc dust and HCl to ethyl propiolate (Baeyer, *B.* 18, 678, 2269).

Tetra-acetylene di-carboxylic acid $C_{10}H_2O_4$ *i.e.* $CO_2H.C{:}C.C{:}C.C{:}C.C{:}C.CO_2H$.

Preparation.—An aqueous solution of the acid sodium salt of di-acetylene di-carboxylic acid is heated on the water-bath. Sodium di-acetylene mono-carboxylate, $H.C{:}C.C{:}C.CO_2Na$, is then formed, with evolution of CO_2; the cuprous compound of this salt, $Cu.C{:}C.C{:}C.CO_2Na$ (?), is then prepared and this is oxidised by potassic ferricyanide:

$$2CuC{:}C.C{:}C.CO_2Na + O_2 = 2CuO + (C{:}C.C{:}C.CO_2Na)_2$$

(Baeyer, *B.* 18, 2271). Tetra-acetylene di-carboxylic acid may be reduced to sebacic acid,

$$CO_2H.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CO_2H,$$

by sodium-amalgam.

Iodo-acetylene carboxylic acid *v.* IODO-PROPIOLIC ACID.

ACETYLENE DI-CHLORIDE *v.* DI-CHLORO-ETHYLENE.

ACETYLENE TETRA-CHLORIDE *v.* TETRA-CHLORO-ETHANE.

ACETYLENE CHLORO-BROMIDE *v.* CHLORO-BROMO-ETHYLENE.

ACETYLENE CHLORO-IODIDE *v.* CHLORO-IODO-ETHYLENE.

ACETYLENE HYDROCHLORIDE *v.* CHLORO-ETHYLENE.

ACETYLENE DI-HYDROCHLORIDE *v.* *di*-CHLORO-ETHANE.

ACETYLENE IODIDE *v.* *di*-IODO-ETHYLENE.

ACETYLENE NAPHTHALENE *v.* ACENAPHTHYLENE.

ACETYLENE-UREA $C_4H_6N_4O_2$ *i.e.*

CO<(NH.CH.NH)(NH.CH.NH)>CO. *Glycoluril.*

S. ·094 at 17°. Formed as white needles when conc. HCl is added to a solution of glyoxal (1 pt.) and urea (2 pts.) and water (3 pts.). If the filtrate is evaporated, it deposits a yellow modification or impure form (Schiff, *A.* 189, 157; Böttinger, *B.* 11, 1787). Also formed by heating a mixture of tri-chloro-lactic acid, urea, and a little water at 100° (Pinner, *B.* 17, 1997). Formed when allantoïn is reduced with (1 p. c.) sodium-amalgam (Reineck, *A.* 131, 119; Widman, B. 19, 2477).

Properties.—White glistening prisms, sol. hot water. Gives a white flocculent pp. with $Hg(NO_3)_2$. Split up by boiling baryta water into urea and hydantoic acid—$C_4H_4Ag_2N_4O_2$.

ACETYL-ETHYL-PROPIONIC ACID *v.* ACETYL-VALERIC ACID.

α-ACETYL-β-ETHYL-SUCCINIC ETHER $C_{12}H_{20}O_5$ *i.e.* CO_2Et[illegible]$.CHAc.CHEt.CO_2Et$ (263°) S.G. $\frac{[illegible]}{17\cdot5}$ 1·004. From aceto-acetic ether (68 g.), alcohol (120 g.), sodium (12 g.) and α-bromo-butyric ether (102 g.) (L. T. Thorne, *C. J.* 39, 336; S. Young, *C. J.* 43, 172).

Reactions.—1. Decomposed by *potash* (2 pts.) and water (1 pt.) into acetic and ethyl-succinic acid.—2. Decomposed by potash (1 pt.) and water (20 pts.) into salts of CO_2 and β-acetyl-α-ethyl-propionic acid (*v.* ACETYL-VALERIC ACID).—3. With NaOEt and MeI it gives α-acetyl-α-methyl-β-ethyl-succinic ether (*q. v.*)—4. The ether (3 pts.) boiled with conc. HCl (2 pts.) and water (4 pts.) for 2 days forms β-acetyl-α-ethyl-propionic acid, which may be extracted by ether, and a crystalline acid, *Ketolactonic acid* (*q. v.*) which remains in the water. Ethyl-succinic acid is also formed.—5. When *heated*, it partly splits up into alcohol and ketolactonic acid.

α-ACETYL-α-ETHYL-SUCCINIC ETHER $C_{12}H_{20}O_5$ *i.e.* $CO_2Et.CAcEt.CH_2.CO_2Et$ (264°). From sodium acetyl-succinic ether and EtI (Huggenberg, *A.* 192, 146). Conc. alcoholic KOH converts it into ethyl-succinic acid.

DI-ACETYL-FUMARIC ETHER $C_{12}H_{16}O_6$ *i.e.* $CO_2Et.CAc{:}CAc.CO_2Et$ [96°]. Formed by the action of iodine (1 mol.) upon di-sodio-di-acetyl-succinic ether (1 mol.) suspended in ether:

$$CO_2Et.CNaAc.CNaAc.CO_2Et + I_2 = CO_2Et.CAc{:}CAc.CO_2Et + 2NaI.$$

Long silky needles (Just, *B.* 18, 2636).

α-ACETYL-GLUTARIC ETHER $C_{11}H_{18}O_5$ *i.e.* $CO_2Et.CHAc.CH_2.CH_2CO_2Et$ (272°) S.G. $\frac{14\cdot1}{17\cdot5}$ 1·0505. From aceto-acetic ether, β-iodo-propionic ether, benzene, and sodium (Wislicenus a. Limpach, *A.* 192, 130). Conc. alcoholic KOH splits it into acetic and glutaric acids. Boiling HCl forms CO_2 and γ-acetyl-butyric acid.

β-Acetyl-glutaric acid $CHAc(CH_2.CO_2H)_2$. [109°]. Formed by heating α-carboxy-β-acetyl-glutaric acid (from chloro-acetyl-propionic ether

and sodio-malonic ether) (Conrad a. Guthzeit, *B.* 19, 44).—AgA′.

Di-acetyl-glutaric ether $C_{13}H_{20}O_6$ *i.e.* $CO_2Et.CHAc.CHAc.CH_2.CO_2Et$ or $CO_2Et.CHAc.CH_2.CO.CH_2.CH_2.CO_2Et$. (c. 245) at 140 mm. From bromo-acetyl-propionic ether, $CH_3.CO.CHBr.CH_2.CO_2Et$ and sodio-aceto-acetic ether (Knorr, *B.* 19, 47). Ammonia in HOAc converts it into di-methyl-pyrryl-acetic carboxylic ether

$$HN\left<\begin{array}{l}CMe:C.CH_2.CO_2Et\\ \quad\quad |\\ CMe:C.CO_2Et\end{array}\right.$$

ACETYL-GLYCOCOLL *v.* ACETURIC ACID.

ACETYLIDE *v.* ACETYL CHLORIDE, *Reaction* 11.

ACETYL IODIDE C_2H_3OI or AcI (108°) (G.); (105°) (C.). S. G. $\frac{17}{}$ 1·98 (O.). Prepared by the action of P and I upon acetic anhydride (Guthrie, *P. M.* [4] (1857) 14, 183) or on KOAc (Cahours (1857) *C. R.* 44, 1253). Also by heating acetyl chloride with $CaI_2 3\frac{1}{2}aq$ at 75°. The water of crystallisation has little saponifying effect (Spindler, *A.* 231, 272).

Properties.—Liquid. Fumes in air; pungent smell; sour taste. Water quickly forms HI and HOAc; alcohol forms EtOAc. Decomposed by zinc or sodium at 15°, and by mercury in sunshine, forming HgI (G.). H. W.

ACETYL-MALONIC ETHER $C_9H_{14}O_5$ *i.e.* $CH_3.CO.CH(CO_2Et)_2$ (239°–245°) S.G. $\frac{22}{}$ 1·080. From aceto-acetic ether, alcoholic NaOEt and $ClCO_2Et$. (Ehrlich, *B.* 7, 892; Conrad, *A.* 214, 35). Aqueous NaOH decomposes it into acetone, CO_2, alcohol, and acetic acid.

ACETYL-METHYL-ACETO-ACETIC ETHER *v.* ACETO-ACETIC ACID.

ACETYL-TETRA-METHYLENE *v.* TETRA-METHYLENE METHYL KETONE.

ACETYL-TETRA-METHYLENE CARBOXYLIC ACID, so called, *v.* ACETYL-BUTYL ALCOHOL.

ACETYL-TRI-METHYLENE *v.* *tri*-METHYLENE METHYL KETONE.

α-ACETYL-α-METHYL-β-ETHYL - SUCCINIC ETHER $C_{13}H_{22}O_5$ *i.e.* $CH_3.CO.CMe(CO_2Et).CHEt.CO_2Et$. From α-acetyl-β-ethyl-succinic ether, NaOEt and MeI (S. Young, *C. J.* 43, 178). Boiled with dilute HCl it forms a γ-oxy-octoic acid (*q. v.*) and methyl-ethyl-succinic acid.

ACETYL-METHYL-TRI-METHYLENE CARBOXYLIC ACID *v.* *propylene-aceto-acetic acid* under ACETO-ACETIC ACID.

α-ACETYL-α-METHYL-GLUTARIC ACID $C_{12}H_{20}O_5$ *i.e.* $CO_2Et.CMeAc.CH_2.CH_2.CO_2Et$.(281°); S.G. $\frac{20}{17.5}$ 1·043. From β-iodo-propionic ether and sodium methyl-aceto-acetic ether (Wislicenus a. Limpach, *A.* 192, 133). With conc. alcoholic KOH it gives acetic and α-methyl-glutaric acids.

ACETYL-METHYL-PYROTARTARIC ETHER *v.* ACETYL-DI-METHYL-SUCCINIC ETHER.

α-ACETYL-α-METHYL-SUCCINIC ETHER $C_{11}H_{18}O_5$ *i.e.* $CO_2Et.CMeAc.CH_2.CO_2Et$ (c. 263°) S.G. 1·067. From sodium acetyl-succinic ether and MeI (Kressner, *A.* 192, 135). Decomposed by conc. alcoholic KOH with formation of acetic and pyro-tartaric acids. Baryta-water or HCl produce CO_2 and β-acetyl-butyric acid (*q. v.*).

α-Acetyl-β-methyl-succinic ether $CO_2Et.CMeH.CAcH.CO_2Et$ (c. 258°) (C.); (c. 263°) (Gottstein, *A.* 216, 31); (c. 227°) at 165 mm. (Bischoff, *A.* 206, 320). S.G. $\frac{17}{17.5}$ 1·061. Formed by action of α-bromo-propionic ether on sodium aceto-acetic ether (Conrad, *A.* 188, 226). Decomposed by conc. KOH into alcohol, pyrotartaric acid, acetic acid, CO_2, and β-acetyl-iso-butyric acid; baryta-water (8 p.c.), or HCl, produce only CO_2 and β-acetyl-iso-butyric acid.

α-Acetyl-α-β-di-methyl-succinic Ether $C_{12}H_{20}O_5$ *i.e.* $CO_2Et.CMeAc.CHMe.CO_2Et$ (270°–272°) S.G. $\frac{17}{17.5}$ 1·057. Formed from α-acetyl-β-methyl-succinic ether, sodium, and MeI (Hardtmuth, *A.* 192, 142). Boiling conc. alcoholic KOH converts it into acetic and α-β-di-methyl-succinic acids.

ACETYL OXIDE and **Peroxide** *v.* ACETIC OXIDE.

ACETYL-OXY-COMPOUNDS *v.* OXY-COMPOUNDS.

ACETYL-PHENYLENE-DIAMINE *v.* PHENYLENE-DI-AMINE.

β-ACETYL-α-PHENYL-PROPIONIC ACID $C_{11}H_{12}O_3$ *i.e.* $CO_2H.CHPh.CH_2Ac$. *Benzyl-acetone-γ-carboxylic acid.* [126°]. Prepared by boiling the ethers of acetyl-phenyl-succinic acid with baryta-water or dilute HCl. Plates. V. sol. alcohol or ether. On reduction with sodium-amalgam it gives the lactone of γ-oxy-α-phenyl-valeric acid, $CH_3.CH(OH).CH_2.CHPh.CO_2H$.

Salts.—$*A'_2Zn$: long white needles.—*AgA′: white pp.—$*CuA'_2$: green; insol. water, sol. alcohol.—$*CuA'_2$ and $*BaA'_2$ are easily soluble (Weltner, *B.* 17, 72).

ACETYL-PHENYL-SUCCINIC ACID $C_{12}H_{12}O_5$ *i.e.* $CO_2H.CHPh.CHAc.CO_2H$. [121°]. Formed by saponification of the di-ethyl-ether, which is prepared by the action of phenyl-bromo-acetic ether on sodio-acet-acetic ether. Large plates. (Weltner, *B.* 17, 71.) When boiled with dilute hydrochloric acid or baryta water, it splits off CO_2, giving acetyl-phenyl-propionic acid, $C_6H_5.CH(CO_2H).CH_2.CO.CH_3$.—$A''K_2$ easily soluble glistening needles.

(α)-*Mono-ethyl-ether* $C_{14}H_{16}O_5$ *i.e.* $CO_2Et.CHPh.CHAc.CO_2H$. [133°]. Formed together with the di-ethyl ether by the action of phenyl-brom-acetic ether upon sodio-aceto-acetic ether. On heating, it evolves CO_2, giving phenyl-levulic ether (Weltner, *B.* 18, 790).

(β)-*Mono-ethyl-ether* $C_{14}H_{16}O_5$ *i.e.* $CO_2H.CHPh.CHAc.CO_2Et$. [128°]. White pearly plates; easily soluble in alcohol and ether. Formed by the action of sodium phenyl-bromo-acetate upon sodio-aceto-acetic ether. By heating to 200° CO_2 is not split off. Boiled with baryta, it yields phenyl-levulic acid. It is reduced by sodium amalgam to α-phenyl-valero-γ-lactone-β-carboxylic acid:

$$\begin{array}{l}CHPh.CO.O\\ \;\;|\quad\quad\quad\;\; |\\ CH(CO_2H).CH.CH_3.\end{array}$$

With alcoholic NH_3 it yields $C_{12}H_{12}N_2O_2$.

Phenyl-hydrazide $C_{22}H_{22}N_2O_4$ [149°], plates.

Di-ethyl-ether $A''Et_2$ [76°], plates.

DI-ACETYL-PHOSPHORIC ACID $C_4H_7PO_6$ *i.e.* $H_3Ac_2PO_5$. A viscid liquid, formed by the action of AcCl on Ag_3PO_4 (Carius a. Kämmerer, *A.* 131, 170). Boiling water decomposes it into acetic and ortho-phosphoric acids. It forms a calcium salt, $CaHAc_2PO_5 2aq$, crystallising in needles.

ACETYL-PIPER - PROPYL - ALKEINE *v.* OXYPROPYL-PIPERIDINE.

ACETYL-PROPIONIC ACIDS $C_5H_8O_3$.

α-Acetyl-propionic Acid $CH_3.CHAc.CO_2H$, *v.* *Methyl-aceto-acetic acid* under ACETO-ACETIC ACID.

β-Acetyl-propionic Acid $CH_3.CO.CH_2.CH_2.CO_2H$. *Levulic acid.* [33·5°]. (239°). S.G. $\frac{15}{}$ 1·135. μ_D 1·443 at 15°. R_∞ 45·3.

Formation.—1. By boiling acetyl-succinic ether with dilute HCl (Conrad, *B.* 11, 2177). 2. By boiling the following substances with very dilute H_2SO_4: Levulose, inulin, cane sugar (Grote a. Tollens, *A.* 175, 181), gum arabic, or caragheen moss (Bente, *B.* 9, 1157). Filter paper and deal shavings give a small quantity. Small quantities may also be got from glucose, milk-sugar, and galactose, by heating with aqueous HCl.

Preparation.—Cane-sugar (1500 g.) is heated for 20 hours with water (1500 g.) and H_2SO_4 (150 g.), with occasional shaking. A large quantity of humic substance separates. The thick liquid is filtered under pressure, mixed with $CaCO_3$ (150 g.), and the whole evaporated (till it weighs 1500 g.). The liquid is again filtered, mixed with H_2SO_4 (50 g.) and shaken with ether. After evaporating the ether, the levulic acid (100 g.) is rectified (Grote, Kehrer a. Tollens, *A.* 206, 210). If glucose be used, the yield is not so good, and it is then better to use HCl (*v.* Conrad a. Guthzeit, *B.* 18, 442). Formic acid is also formed in these reactions:

$$C_6H_{12}O_6 = C_5H_8O_3 + CH_2O_2 + H_2O.$$

Properties.—Deliquescent trimetric plates. V. sol. water, alcohol or ether. On distillation it produces (α)- and (β)-angelico-lactone, and also acetic acid, and another acid possibly $C_{10}H_{10}O_3$ [208°] (Wolff, *A.* 229, 260). Not attacked by bromine in the cold.

Reactions.—1. *Chromic mixture* produces CO_2 and acetic acid.—2. Dilute HNO_3 gives succinic, oxalic, acetic, and hydrocyanic acids (Tollens, *B.* 12, 334; *A.* 206, 257).—3. Reduced, by P and HIAq at 150°-200°, or by sodium-amalgam in acid solution, to *n*-valeric acid.—4. In alkaline solution *sodium amalgam* produces γ-oxy-valeric acid (*q. v.*). 5. Gives the iodoform reaction with NaOH and I.—6. Reacts with hydroxylamine, forming an oxim.

Salts.—$CaA'_2$2aq: minute needles.—AgA': six-sided tables.—NaA': minute needles.—CuA'_2 (at 150°): bluish-green flat needles or prisms. Barium, magnesium, and cadmium salts are gummy.

Ethers.—MeA'. (191·5°). S.G. $\frac{0}{0}$ 1·0684. μ_D 1·4216 at 15°. R_∞ 52·2.—EtA'. (200·5°) (G. K. a. T.) (204°) (W.). S.G. $\frac{0}{0}$ 1·0325. μ_D 1·421. R_∞ 60·2. —PrA'. (215·5°). S.G. $\frac{0}{0}$ 1·0103. μ_D 1·4246. R_∞ 69·5.

Amide.—$C_5H_7O.NH_2$. [108°]. From ethyl levulate and alcoholic NH_3 or from (α)-angelico-lactone (*q. v.*) and aqueous or alcoholic ammonia. Six-sided tables (from alcohol-chloroform, Wolff, *A.* 229, 260).

References.—See also BROMO- and CHLORO-ACETYL-PROPIONIC ACIDS.

ACETYL-PROPYL ALCOHOL $C_5H_{10}O_2$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2OH$. *Methyl γ-oxy-propyl ketone.* A colourless liquid, soluble in water, formed by boiling bromo-ethyl-aceto-acetic ether $BrCH_2CH_2.CHAc.CO_2Et$ with dilute HCl. It readily reduces ammoniacal $AgNO_3$Aq but not Fehling's solution. It is converted by heat into an anhydride. *Sodium-amalgam* reduces it to α-γ-di-oxy-*n*-pentane, $CH_3.CH(OH).CH_2.CH_2.CH_2OH$ (Perkin jun. a. Freer, *B.* 19, 2566).

ACETYL-PYRO-PHOSPHORIC ACID.

The barium salt, $BaHAcP_2O_7$2aq, is got as a crystalline pp., sl. sol. dilute acids, by adding aqueous hydrogen peroxide to a solution of barium acetyl-pyrophosphite (Menschutkin, *A.* 136, 254).

ACETYL - PYRO - PHOSPHOROUS ACID, $AcH_3P_2O_5$2aq, is got by heating AcCl with H_3PO_3 at 50° (Menschutkin, *A.* 133, 317). Crystalline mass.

Salts.—$K_2HAcP_2O_5$2½aq: slightly sol. water. $BaHAcP_2O_5$: insol. water.—$PbHAcP_2O_5$: insol. water.

ACETYL-PYRO-TARTARIC ACID *v.* ACETYL-METHYL-SUCCINIC ACID.

ACETYL-PYRROL *v.* PYRROL.

Pseudo-acetyl-pyrrol *v.* PYRRYL METHYL KETONE.

ACETYL-SUCCINIC ETHER $C_{10}H_{16}O_5$ *i.e.* $CO_2Et.CHAc.CH_2.CO_2Et$. (c. 255°); (210° i. V.) at 330 mm. S.G. $\frac{21}{17\cdot5}$ 1·079; $\frac{15}{15}$ 1·088; $\frac{25}{25}$ 1·080. M.M. 10·343 (Perkin, *C. J.* 45, 517). Formed by action of chloro-acetic ether upon sodium aceto-acetic ether (Conrad, *A.* 188, 218). Oil. Sol. alcohol or ether. Gives no colour with Fe_2Cl_6. Conc. alcoholic KOH splits it into acetic and succinic acids; boiling baryta-water forms β-acetyl-propionic ether and CO_2.

Phenyl-hydrazide $C_{16}H_{22}N_2O_4$. [80°]. At 150° it splits off EtOH and gives methyl-oxy-quinizyl-acetic ether (Knorr a. Blank, *B.* 17, 2051).

Di-aceto-succinic Ether $C_{12}H_{18}O_6$ *i.e.* $CO_2Et.CHAc.CHAc.CO_2Et$. [79°].

Sodium acetacetic ether is treated in ethereal solution with iodine (Rügheimer, *B.* 7, 892):

$$2CO_2Et.CHNa.CO.CH_3 + I_2 = (CO_2Et.CHAc)_2 + 2NaI.$$

The ethylic di-aceto-succinate crystallises from the ether (Harrow, *C. J.* 33, 427). It forms trimetric tables, v. e. sol. alcohol, ether, or benzene.

Reaction.—1. Boiled with dilute H_2SO_4 (1 : 10) it gives off CO_2 and forms pyro-tritaric or uvic ether $C_9H_{12}O_3$ and carbo-pyro-tritaric ether $C_8H_7O_3Et$.—2. *Hydroxylamine* forms a di-oxim (needles; Münchmeyer, *B.* 19, 1849), and a neutral ether $C_{12}H_{17}NO_5$ (Knorr, *B.* 18, 1568).—3. *Ammonia* forms di-methyl-pyrrol di-carboxylic ether $C_4HMe_2N(CO_2Et)_2$ or

$$NH\left\langle\begin{array}{l} CMe:C.CO_2Et \\ \qquad\quad | \\ CMe:C.CO_2Et. \end{array}\right.$$

Primary bases act in a similar manner, thus methylamine forms

$$NMe\left\langle\begin{array}{l} CMe:C.CO_2Et \\ \qquad\quad | \\ CMe:C.CO_2Et \end{array}\right.$$

(Knorr, *B.* 18, 299). 4. *Phenyl-hydrazine* acts in a similar way: $C_{12}H_{18}O_6 + N_2H_3C_6H_5 = C_{18}H_{22}N_2O_4 + 2H_2O$. The new compound, which may be

$$\begin{array}{l} NPh.CMe:C.CO_2Et \\ \;| \qquad\qquad | \\ NH\;\; .CMe:C.CO_2Et \end{array}$$

is called phenyl-di-methyl-pyridazine di-carboxylic ether. It contains H_2O less than the mono-phenyl-hydrazide of di-acetyl-succinic ether, $CO_2Et.CH(CMe:N_2PhH).CHAc.CO_2Et$ (Knorr, *B.* 17, 2058; 18, 305). It crystallises in prisms, [127°] (from benzoline). See also PHENYL-HYDRAZINE.

ACETYL SULPHIDE $C_4H_6O_2S$ or Ac_2S. *Di-acetyl sulphide, Thio-acetic anhydride* (120°).

Preparation.—1. From Ac_2O and P_2S_5 (Kekulé, *A.* 90, 312). Yield 10 p.c.—2. From AcCl and K_2S.—3. By distilling PbSAc.

Properties.—An oil, slowly decomposed by water into HOAc and HSAc.

Di-acetyl Di-sulphide $C_4H_6O_2S_2$ or Ac_2S_2 [21°].

Formation.—1. From KSAc and I (Kekulé a. Linnemann, *A.* 123, 279).—2. From BaO_2 and Ac_2S in ethereal solution (Beckmann, *J. pr.* 125, 465): $2Ac_2S + BaO_2 = Ac_2S_2 + Ba(OAc)_2$.—3. By electrolysis of thio-acetic acid (Bunge, *B.* 3, 297).

Properties.—Crystalline. Insol. water, v. sol. alcohol or CS_2. Decomposed by warm water or by alkalis forming thio-acetic acid and sulphur. Decomposed by distillation.

ACETYL SULPHOCYANIDE C_3H_3NSO or $CH_3.CO.S.Cy$. (133°). S.G. $\frac{16}{}$ 1·151. From AcCl and lead sulphocyanide (Miquel, *A.Ch.* [5] 11, 295). Pungent liquid. Decomposed by water into HOAc and HSCN. Forms with NH_3 in ethereal solution a non-volatile liquid which dissolves in water and gives a red colour with Fe_2Cl_6.

ACETYL-THIO-UREA *v.* Thio-urea.

ACETYL-TOLYLENE-DI-AMINE *v.* Tolylene-di-amine.

ACETYL-UREA *v.* Urea.

ACETYL-VALERIC ACID $C_7H_{12}O_3$.

α-Acetyl-*n*-valeric Acid *v. n-propyl-aceto-acetic acid* under Aceto-acetic acid.

α-Acetyl-*s*-*iso*-valeric Acid *v. iso-propyl-aceto-acetic acid* under Aceto-acetic acid.

α-Acetyl-*u*-*iso*-valeric Acid *v. methyl-ethyl-aceto-acetic* acid under Aceto-acetic acid.

β-Acetyl-*u*-*iso*-valeric Acid

$CH_2Ac.CHEt.CO_2H$.

(250°-252°). Got by boiling α-acetyl-β-ethyl-succinic ether (*q. v.*) with dilute KOH (Thorne, *C.J.* 39, 340). Liquid, miscible with water, alcohol, and ether. Turns brown in air. It is gradually decomposed by heat into H_2O and an oil $C_7H_{10}O_2$ (219°). S.G. $\frac{2}{2}\frac{1}{0}$ 1·0221.

Reaction.—HNO_3 oxidises it to ethyl-succinic acid.

Salts.—Gummy, soluble in water.

Ether.—EtA' (224°-226°). Lighter than water.

ACHILLEA.—The Iva plant (*A. Moschata*) has been chemically examined by v. Planta-Reichenau (*A.* 155, 145), who has extracted from it the following substances: 1. Ivaïn $C_{24}H_{42}O_5$, obtained by distilling the dried herb (freed from the roots) with water to remove volatile oil, exhausting the dried residue with absolute alcohol, precipitating with lead acetate, removing excess of lead with H_2S, and exhausting the evaporated residue with acetic acid to remove achillein and moschatin. Ivaïn then remains as a dark yellow resinous mass, insoluble in water, easily soluble in alcohol, yielding an intensely bitter solution. — 2. Achilleïn $C_{20}H_{38}N_2O_{15}$ and Moschatin $C_{21}H_{27}NO_7$ are obtained by distilling the herb, gathered before flowering, with water, exhausting the concentrated filtrate with absolute alcohol, evaporating off the alcohol and adding water, which throws down moschatin; and on treating the liquid filtered therefrom with $Pb(OH)_2$, again filtering, removing lead with H_2S, and evaporating, Achilleïn remains as a brown-red mass, very soluble in water, less readily in alcohol, insoluble in ether; very bitter; not precipitated by lead salts. Resolved by prolonged boiling with dilute sulphuric acid into sugar and achilletin $C_{11}H_{17}NO_4$, a dark-brown powder, insoluble in water, very slightly soluble in alcohol; not bitter. Moschatin $C_{21}H_{27}NO_7$ is pulverulent, nearly insoluble in water, somewhat soluble in absolute alcohol; tastes bitter.

A. Ageratum, growing in Italy and Provence, yields an essential oil boiling at 165°-182°; sp. gr. 0·849 at 14° (De Luca, *J. Ph.* [4] 18, 105).
H. W.

ACHROO-DEXTRIN *v.* Dextrin and Starch.

ACIDIMETRY. The estimation of acids by volumetric methods. *V.* Analysis.

ACID-FORMING OXIDES. Same as Anhydrides (*q. v.*).

ACIDS.—*Salts of hydrogen.* The word *acid* (*ac*, sharp; *acere*, to be sour; compare *acetum*, vinegar, ὀξύς, ὄξος) was originally loosely applied to all sour liquids. The term cannot now be accurately defined; but it may be stated generally that an acid is a compound of hydrogen, which, when mixed with, or dissolved in, water, is capable of exchanging the whole, or a portion, of the hydrogen it contains for a metal, with simultaneous formation of water, by the action on the aqueous solution of the acid of a metallic oxide or hydroxide.

History.—The corrosive action of acids, and their power of dissolving metals and other substances have been known from early times. Thus Geber, who lived during the eighth century, was acquainted with impure nitric and sulphuric acids, and described them under the name *aquæ dissolutivæ*. Paracelsus (16th century), from whom the school of Iatro-chemists sprang, held that the human body in health consisted of certain acid and alkaline principles which balanced each other, and that disease was due to a preponderance of one or other of these principles. He was the first to propound a theory to account for the properties common to all acids; he supposed that they all contained an acid principle, which conferred taste and solubility on all substances into which it entered. This theory was accepted by Becher (17th century), who named the acid principle *acidum primogenium*; and he added that it consisted of a compound of earth and water, both of which he believed to be elements. The distinctive properties of acids:—their solvent power, their power of changing the colour of certain vegetable tinctures, and the fact that they form neutral bodies with alkalis;—were catalogued by Boyle (17th century). Stahl, in 1723, adopted Becher's theory, and endeavoured to prove that while acids were the bases of all saline bodies, the principle of all acids was sulphuric acid. Stahl's view continued to find supporters for a long time, but its defects were at length perceived. Many of the supporters of the phlogistic theory held that inorganic acids, such as sulphuric and phosphoric acids, were simple substances; and that by their combinations with phlogiston they gave rise to bodies such as sulphur and phosphorus, which were then regarded as compounds, but which we now know to be elements. After the discovery of oxygen by Priestley and Scheele, Lavoisier, in naming that element from ὀξύς (acid) and γεννάω (I produce), generalised

**the facts discovered by him, that many acid bodies are produced by the union of 'combustibles' with oxygen; and although it was pointed out by Berthollet in 1789 that sulphydric and prussic acids contain no oxygen, the view of Lavoisier generally prevailed until the researches of Davy, and of Gay-Lussac and Thenard, on muriatic and oxymuriatic acids (hydrochloric acid and chlorine) in 1810, and the discovery and examination of hydriodic acid, and the investigation of prussic acid by Gay-Lussac in 1814 and 1815, compelled chemists to recognise the existence of true acids containing no oxygen, and led to a distinction being drawn between acids which contained oxygen, and those which did not.

Lavoisier also regarded acids as binary oxygenated compounds; and he supposed that the water which must be present in order that an acid shall react on other bodies merely played the part of a solvent. This view was supported and extended by Berzelius, who taught that certain oxides are capable of uniting with each other to form 'ternary' compounds or salts, and that these salts are decomposed by electrolysis into their 'binary' constituents, which are an acid and a base. Berzelius therefore applied the term electronegative to that oxide which appeared at the positive electrode on electrolysis of a salt, and the term electropositive to that oxide which separated at the negative electrode. The negative oxides he classed as acids, and the positive oxides as bases. This theory ignored the fact that water is associated with these oxides in their various reactions; and, moreover, it overlooked the evident analogy between acids containing oxygen and acids containing no oxygen, but formed by the union of the halogens, or haloid groups, with hydrogen. To restore this analogy, Davy proposed to abandon the old view that acids were compounds of certain elements with oxygen, and suggested that all acids, whether they contained oxygen or not, should be considered as compounds of hydrogen. Dulong supported Davy's view, and extended it; he regarded acids as compounds of hydrogen with elements such as Cl, I, S; or with radicles such as CN, NO_3, SO_4. As it was at that time supposed that such radicles were capable of separate existence, and as Dulong's hypothesis involved the creation of a large number of hypothetical substances, this hypothesis did not meet with general support. It was reserved for Gerhardt, led by a study of organic substances, to prove that most acids, when vaporised, do not separate into an oxide and water, but pass into the state of vapour as a whole. From this it followed that hydrogen, replaceable by metals, must be a constituent of all true acids.

Characteristic features of acids.—Bodies possessing properties corresponding with the definition of an acid given at the beginning of this article always contain hydrogen in intimate combination with one or more of the following elements; fluorine, chlorine, bromine, iodine, oxygen, sulphur, selenion, tellurium, or certain groups of elements (*e.g.* cyanogen) of which carbon is one (comp. Acids, Organic, p. 53). It is true that water is not accounted an acid, nor is it usual to include hydrogen dioxide among the acids; yet if the definition of acid were strictly applied hydrogen dioxide would find a place in this class, for it has an acid reaction with test paper, and on addition, for example, of barium hydroxide to a solution of it in water, the reaction characteristic of acids takes place;—

$$Ba(OH)_2.8H_2O + H_2O_2 = BaO_2.8H_2O + 2H_2O.$$

Again, the reactions of hydrogen sulphide, selenide, and telluride, with alkalis, would lead to their inclusion among acids. The name acid must also be applied to most compounds of hydrogen and one of the elements above mentioned with a third element. The following examples will illustrate the definition given:—

Simple.	Compound.
HF.	$HBF_4 = HF.BF_3$.
HCl.	$H_2PtCl_6 = 2HCl.PtCl_4$.
HCN.	$H_4Fe(CN)_6 = 4HCN.Fe(CN)_2$.
(H_2O.)	$H_2SO_4 = H_2O.SO_3$.
H_2S.	$H_2CS_3 = H_2S.CS_2$.
&c.	&c.

Such bodies as H_2ZnO_2 ($Zn(OH)_2$), and H_3AlO_3 ($Al(OH)_3$), may be classed either among acids or basic hydroxides, inasmuch as they possess the characteristics of both classes.

Among the compounds of carbon the acids form an important class. The formulæ of these compounds may be supposed to be derived from the formula either of formic acid, or of carbonic acid. If formic acid be taken as the type, then most acids containing carbon may be viewed as substituted formic acid; thus:—

HCOOH.	CH_3COOH.	$C_2H_4(COOH)_2$.
Formic acid.	Acetic acid.	Succinic acid.

$C_3H_4(OH)(COOH)_3$.
Citric acid.

It is to be noticed that in two cases more than one molecule of formic acid is employed; and that succinic acid, by this view, is to be regarded as two molecules of formic acid, in which two atoms of hydrogen are replaced by the group C_2H_4; while citric acid is derived from three molecules of formic acid by replacement of three atoms of hydrogen by the group $C_3H_4(OH)$. The carboxylic acids may be similarly derived from carbonic acid ($CO(OH)_2$), if one hydroxyl group be regarded as replaced by an alkyl or similar group. But it is clear that unless this view of the composition of carbon acids helps to render prominent the actual relations existing between these compounds, it can be of no value. In this view of the constitution of carbon acids these compounds are all represented as containing the characteristic group CO.OH; this group has been named 'carboxyl,' a word derived from 'carbonyl,' CO, and 'hydroxyl,' OH, and implying the presence of these two groups. That most of the acids of carbon contain the group CO.OH is rendered probable by the following considerations: when one of these acids is distilled with phosphorous chloride, PCl_3, the hydroxyl group is replaced by chlorine, thus;

$$3CH_3.CO.OH + 2PCl_3 = 3CH_3CO.Cl + P_2O_3 + 3HCl.$$

And on warming such a chloride with water the acid is re-formed;

$$CH_3.CO.Cl + H_2O = CH_3CO.OH + HCl.$$

It is thus proved that oxygen and hydrogen can be removed together from the acid molecule. Moreover, on treatment of the acid chloride with**

nascent hydrogen, the chlorine is replaced by hydrogen, and an aldehyde is produced, thus;

$$CH_3COCl + 2H = CH_3CHO + HCl.$$

This aldehyde, when treated with phosphoric chloride, PCl_5, exchanges its oxygen for two atoms of chlorine, thus;

$$CH_3CHO + PCl_5 = CH_3.CHCl_2 + POCl_3.$$

It is therefore inferred that the atom of oxygen replaced by chlorine in the last reaction is differently related to the other atoms in the molecule from that atom of oxygen which is replaceable by chlorine only when hydrogen accompanies it. The formula of the characteristic group, CO.OH, thus appears reasonable.

But there are many compounds of carbon exhibiting the property of exchanging hydrogen for a metal by the action of an oxide or hydroxide, which do not contain the carboxyl group. Among these compounds may be mentioned bodies such as ethane sulphonic acid, $C_2H_5.HSO_3$, and ethane phosphonic acid, $C_2H_5.H_2PO_3$, &c.; many of these bodies may be regarded as acid ethereal salts of inorganic acids. There are, however, others which, in spite of their acid properties, it is not usual to name acids, although many of them might be legitimately included in this class. For instance the mercaptans, of which ethyl hydrosulphide may be chosen as an example, react with oxides or hydroxides in a similar manner to sulphydric acid, H_2S, thus, $C_2H_5.SH + KOH = C_2H_5SK + H_2O$: and the corresponding selenion and tellurium compounds exhibit a like behaviour. Again, many of the nitro-compounds of the alkyl radicles have the power of exchanging hydrogen for a metal, under the usual limitations, as for example:

$$CH_3NO_2 + KOH = CH_2KNO_2 + H_2O:—$$

$C(NO_2)_3H$ yields $C(NO_2)_3K$, etc. Hydroxyquinones, such as alizarin $C_{14}H_6O_2(OH)_2$, act as dibasic acids, forming compounds such as $C_{14}H_6O_2(OK)_2$; phenols, and their substitution derivatives, also yield metallic derivatives, *e.g.* sodium phenate C_6H_5ONa, sodium picrate $C_6H_2(NO_2)_3$ ONa. On comparing such compounds with each other, and with other acids, the following deductions may be drawn:—(1.) That a powerfully electro-negative element such as fluorine, chlorine, bromine, or iodine, confers acid properties on its compound with hydrogen. (2.) That in compounds of elements exhibiting less markedly electronegative properties than the halogens, the presence of an electronegative element is necessary to the development of acid character. This may be seen from the following considerations. Hydrocarbons, such as methane, CH_4, exhibit no acid properties; if an atom of an electronegative element such as oxygen or sulphur is introduced into the molecule in place of one or more atoms of hydrogen, the compound so formed, although not generally a true acid, yet exhibits a more or less acidic character. Thus, methylic alcohol, CH_3OH, forms metallic derivatives (CH_3ONa, &c.) by the action on it of strongly positive metals; but as such compounds are decomposed by water, they cannot be formed in presence of that substance. Here, however, we may note that phenol, C_6H_5OH, and similar compounds, reacts with the hydroxides of strongly positive metals to form metallic derivatives which, although comparatively unstable, are nevertheless capable of existence in presence of an excess of alkaline hydroxide. But if a derivative of a hydrocarbon contain two or more electronegative atoms or groups of atoms in the molecule, then, as a rule, this compound forms metallic derivatives of considerable stability. Thus, the replacement of two atoms of hydrogen in the molecule of an alcohol by an atom of oxygen (converting the group characteristic of primary alcohols, CH_2OH, into the carboxyl group, CO.OH) is attended by a marked increase of acid properties. Similarly the existence of oxygen combined with carbon in hydroxyquinones (as carbonyl, CO) confers on hydroxyl groups present the power of exchanging their hydrogen for metals by reactions common to acids. And in presence of a large amount of an electronegative element the exchangeable hydrogen need not even be present as hydroxyl; for as shown above, such bodies as nitromethane, CH_3NO_2, form metallic derivatives, like CH_2KNO_2. Comp. ACETO-ACETIC ACID, p. 17. Regarding the relations between the nature of different elements and the acidic character of their compounds *v.* further CLASSIFICATION.

BASICITY OF ACIDS.—Some acids, on treatment with the oxide or hydroxide of an alkali metal, may exchange all their hydrogen for metal, thus producing a salt; and it may not be possible to obtain from them a body intermediate between the salt and the acid; such an intermediate derivative is usually termed an acid salt. From other acids such intermediate derivatives are obtainable. The acids of the former class are termed 'monobasic'; those of the latter class are termed 'polybasic,' including the terms 'di-' 'tri-' 'tetra-' basic. The conception of the basicity of acids was introduced by Graham. Before his researches in 1833, it was supposed that an 'acid salt' contained, as its name implies, both acid and salt, and on the binary theory it was considered to be a compound of the two. But Graham showed that in neutral potassium phosphate there are, as he expressed it, three equivalents of potash for one equivalent of phosphoric acid, or in modern language, three atoms of potassium for one atomic group PO_4; and that the acid phosphates differ from the neutral phosphate in containing water instead of potash, or as we should say, hydrogen in place of potassium. The composition of hydrated phosphoric acid being expressed by the symbol (old notation) $PO_5.3HO$, the composition of its different salts might be expressed by the symbols:

$$PO_5.2HO.KO;\ PO_5.HO.2KO;\ PO_5.3KO.$$

Phosphoric acid was therefore termed by Graham a 'tribasic acid.' In 1838, Liebig pointed out the necessity of considering the following acids as polybasic, because of the fact that they form acid as well as neutral salts;—cyanuric, malonic, comenic, citric, aconitic, aconic, tartaric, malic, and fumaric. In consequence of this change of view, Liebig argued that it was better to give up the binary theory of acids held by Berzelius, and to go back to the older theory of Davy, viz. that acids are to be regarded as formed by the combination of hydrogen with a simple or a compound radicle, the nature of this radicle having no part in determining the number of stages in which the replacement of hydrogen by metal takes place. Thus by addition of oxygen or sulphur to sulphuretted

hydrogen (sulphydric acid) the following dibasic acids are obtainable:—

Sulphydric acid . .	H_2S
Hyposulphurous acid .	H_2SO_2
Sulphurous acid . .	H_2SO_3
Sulphuric acid . . .	H_2SO_4
Thiosulphuric acid . .	$H_2S_2O_3$
Dithionic acid . . .	$H_2S_2O_6$

It was, however, known that many acids, having a claim to be considered monobasic, such as hydrofluoric, acetic, benzoic, and stearic, gave rise to double salts by addition of a molecule of acid to a molecule of salt. Laurent and Gerhardt pointed out that the relative densities, in the gaseous state, of many acids belonging to this class imply that a molecule of each acid contains only one atom of hydrogen; further, that an acid of this class forms only one alkyl (or ethereal) salt, and one amide; that while polybasic acids generally yield anhydrides by some direct process, often by the action of heat alone, the anhydrides of monobasic acids are usually obtained indirectly, and that anhydro-salts such as dichromate of potassium, are obtainable only from polybasic acids.

The number of atoms of hydrogen contained in a molecule of an acid is no criterion of its basicity; this fact was noticed by Gerhardt, but its bearings were more fully elucidated by Wurtz and by Kekulé. The basicity of an acid is determined, not by the number of atoms of hydrogen which it contains, but by the number of stages in which the hydrogen can be replaced, or in other words, by the number of salts which it is capable of forming with a specified monovalent metal. Thus a study of the salts of the following acids has led to their classification as shown below.

Monobasic.—HF, HCl, HNO_3, $H(H_2PO_2)$, $H(HCO_2)$, HBF_4, $HAuCl_4$.
Dibasic.—H_2SO_4, $H_2(HPO_3)$, $H_2C_2O_4$, H_2PtCl_6, $C_2H_4(COOH)_2$.
Tribasic.—H_3PO_4, $H_3Fe(CN)_6$, H_3AsO_4, $C_3H_4(OH)(COOH)_3$, $C_3H_3N(COOH)_3$
Tetrabasic.—$H_4P_2O_7$, $H_4Fe(CN)_6$, $C_6H_2(COOH)_4$.
Hexabasic.—$C_6(COOH)_6$.

The number of salts of a monovalent metal which an acid is capable of forming corresponds, as a rule, with its basicity. Thus tribasic orthophosphoric acid forms three salts with potassium, viz. H_2KPO_4, HK_2PO_4, and K_3PO_4; and similarly with other acids.

This classification, as already stated, is founded on a study of the salts of acids containing monovalent metals, practically of the salts formed by the action of potash or soda on the acids. The researches of Thomsen on the quantities of heat produced when acids and bases mutually react in equivalent quantities have confirmed the conclusions drawn from a study of the composition of salts. The principle of the thermal method may be thus stated:—If a dilute aqueous solution of a monobasic acid is mixed with an equivalent quantity of an alkali also in dilute aqueous solution, a definite quantity of heat is produced; if more than one equivalent of acid is used for one equivalent of base, the same quantity of heat is produced. This is shown by the examples which follow:[1]

[1] Figures represent gram-units of heat.

Acid.	Number of equivalents of acid to one equivalent of base (NaOHAq)		
	2	1	$\frac{1}{2}$
HCl.HBr.HI	13,700	13,700	6,850
HF. . .	16,000	16,300	8,200
HSH . .	7,700	7,700	3,900
HNC . .	2,800	2,800	1,400
HNO_3 . .	13,600	13,700	6,800
HPH_2O_2 .	15,400	15,200	7,600
HPO_3 . .	14,200	14,400	—
$H.C_2H_3O_2$.	13,200	13,200	8,600

In most of these instances, the acid forms no acid salt; its hydrogen is replaceable in only one stage. But although acid salts of acetic acid (*e.g.*, $C_2H_4O_2.C_2H_3NaO_2$), and of hydrofluoric acid (HF.KF), are known, the formation of these salts by the action of the neutral salt and the acid is accompanied by a very small thermal change. This fact forms a reason, in addition to those adduced by Gerhardt, for classing hydrofluoric and acetic acids with the monobasic acids.

The thermal value of the action of a base on a polybasic acid, unlike that of the action of a base on a monobasic acid, is dependent on the proportion between the number of equivalents of base and acid used. This is shown by the following examples:

Acid.	Number of equivalents of acid to one equivalent of base (NaOHAq).					
	2	1	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$	$\frac{1}{6}$
H_2SO_4 .	14,200	14,600	15,500	—	7,800	—
H_2SO_3 .	—	15,900	14,500	—	7,300	—
H_2PHO_3 .	14,900	14,800	14,200	9,600	—	—
H_2CO_3 .	—	11,000	10,100	—	—	—
H_3PO_4 .	14,700	14,800	13,500	11,300	—	5,900
$H_4P_2O_7$.	—	14,400	14,300	—	13,200	9,100

Again, a small thermal change is noticed when solutions of a monobasic acid and of the potassium or sodium salt of this acid mutually react; but if a solution of a polybasic acid is allowed to react with a solution of a neutral salt of the same acid, a marked thermal change occurs. Thus the formation of $KHSO_4$ from K_2SO_4 and H_2SO_4 at 23° is accompanied by the disappearance of about 8,000 gram-units of heat.

Ortho-acids and Anhydro-acids.—The acids containing oxygen have been most completely investigated, owing to the fact that most of them are stable at ordinary temperatures, and in presence of air and water. It is inferred that in these acids oxygen and hydrogen are in intimate union, forming a hydroxyl group; the chief reason for this view, *viz.*, that when these acids are treated with phosphorous, or phosphoric, chloride they yield the chloride of the acid radicle, has already been stated. Thus sulphuric acid, $SO_2(OH)_2$, yields sulphuryl chloride, SO_2Cl_2; and phosphoric acid, $PO(OH)_3$, yields phosphoryl chloride, $POCl_3$. Such groups as SO_2, sulphuryl, or PO, phosphoryl, are termed acid radicles, and their compounds with hydroxyl are acids. The term ortho-acid is employed especially in the nomenclature of carbon acids.

An ortho-acid, strictly speaking, is one in which the element to which the hydroxyls are

united is not combined with any other oxygen. Such compounds are in most cases unknown, but their existence is inferred from that of their metallic or ethereal salts, *e.g.* $Si(ONa)_4$; $C(OCH_3)_4$; $CH_3C(OC_2H_5)_3$, &c.

Many of the commonly occurring acids may be regarded as derived from such ortho-acids by removal of water; thus looked at, these acids are partial anhydrides. Their formation is illustrated by the following examples:

$S(OH)_6$ Unknown.	$SO(OH)_4$ Unknown.	$SO_2(OH)_2$ Sulphuric acid.	SO_3 Sulphuric anhydride.
$I(OH)_7$ Unknown.	$IO(OH)_5$ Periodic acid.	$IO_2(OH)_3$ Salts known.	$IO_3(OH)$ Salts known.	I_2O_7 Periodic anhydride (? known)
$P(OH)_5$ Unknown.	$PO(OH)_3$ Orthophosphoric acid.	$PO_2(OH)$ Metaphosphoric acid.	P_2O_5 Phosphoric anhydride.

Partial anhydrides are sometimes also formed by the condensation-products of two or more molecules of an acid, with removal of water, thus:

$$\begin{matrix} S(OH)_5 & & SO(OH)_3 & & SO_2(OH) \\ \rangle O & & \rangle O & & \rangle O \\ S(OH)_5 & & SO(OH)_3 & & SO_2(OH). \end{matrix}$$

Unknown. Unknown. Pyrosulphuric acid.

In most cases the composition of such acids is inferred from that of their salts; the very numerous natural silicates may be conveniently classified as salts of such condensed acids (*v.* SILICATES).

AFFINITY (or *avidity*) OF ACIDS.—By measuring the thermal changes which occur when one equivalent of an acid, in dilute aqueous solution, reacts on one equivalent of the neutral salt of another acid, also in dilute aqueous solution, it is possible to determine the proportion in which the base divides itself between the two acids. Measurements have been made by Thomsen, and he has named the proportion in which the base combines with either acid, the *relative avidity* of the acid. Thus when hydrochloric acid (36·4 parts) is added to potassium nitrate (101 parts), both in dilute aqueous solution, the thermal changes which occur point to an equal partition of the base between the two acids; *i.e.* half the potassium exists in the solution as chloride, and half as nitrate. On mixing nitric acid (63 parts) with potassium chloride (74·4 parts), the heat-change points to the same equal partition of the base. Hence it is concluded that the relative avidity, or affinity, of hydrochloric and nitric acids for potash is equal, and is expressed by the number 0·5. The relative avidity seems to be independent of the nature of the base within certain limits; it is also modified only to a small extent by the concentration of the reacting liquids, or by small changes of temperature. This conclusion of Thomsen has received thorough confirmation by the researches of Ostwald; and this is the more valuable inasmuch as Ostwald measured the partition of acids between bases by a method depending on the alteration of volume attending the mixture of an acid with the salt of another acid. The following table gives the relative affinities of some acids towards the base soda; the affinity of hydrochloric acid being taken as unity:—

Acid	HCl	HBr	HI	HF
Avidity	1	0·89	0·79	0·05
Acid	HCN	$\frac{H_2SO_4}{2}$	$\frac{H_2SeO_4}{2}$	
Avidity	very small	0·49	0·45	
Acid	HNO_3	$\frac{H_3PO_4}{2}$	$\frac{H_2B_2O_4}{2}$	$CCl_3.COOH$
Avidity	1	0·25	very small	0·36
Acid	$(COOH)_2$	$C_4H_6O_6$	$C_2H_4O_2$	
Avidity	0·24	0·05	0·03	

For more details *v.* AFFINITY, p. 67; ACIDS, BASICITY OF, p. 51. Regarding acids *v.* also CLASSIFICATION. An acid with a large avidity or affinity is frequently now spoken of as a *strong acid*, the term *weak* being applied to those acids the affinities of which are expressed by small numbers.

References.—Lavoisier, *Traité élémentaire de Chimie*, ed. 1789, i. 69 *et passim*; Kopp, *Geschichte der Chemie*, i. 308; iii. 17; Davy, *Journal of Science and the Arts*, i. 285; also *G. A.* 54, 377; *T.* 1815, 212; Berzelius, *J.* 6. 184; Graham, *T.* 1833, 253; *P. M.* 3. 451 and 469; Liebig, *A.* 26. 138, 170; *A. Ch.* 68. 5, 70; Laurent, *A. Ch.* [3] 24, 163; *Méthode de Chimie* (1854), 62, *Translation of Cavendish Soc.*, 39–45; Gerhardt, *Gerh.* (1856), 4. 641; Wurtz, *A. Ch.* [3] 55. 466; 56, 342; 61. 161; Kekulé, *A. Ch.* 60, 127; Odling, *P. M.*, 18. 368; Thomsen, *Thermochemische Untersuchungen*, i.; *P.* 138. 65, 208, 498; 139. 193; 140. 88, 530; Berthelot, *C. R.* 75. 264, 435, 480, 538, 583; 87. 671.

W. R.

ACIDS, BASICITY OF.—It has been shown in the art. ACIDS (*q. v.*) that some acids react with the hydroxide (or oxide) of potassium or sodium to form only one salt, whereas other acids by a similar reaction produce more than a single salt. The former acids are called monobasic, the latter polybasic. It was also shown in the art. ACIDS that the basicity of an acid may be determined by an examination of the *heat of neutralisation* of the acid. The thermal value of the reaction of a monobasic acid with a base, in dilute aqueous solutions, is independent of the ratio between the numbers of equivalents of acid and base used, provided not less than one equivalent of base is mixed with a single equivalent of acid; but the thermal value of the reaction of a polybasic acid with a base varies according as 1, 2, 3, &c. equivalents of base react with one equivalent of acid. If the thermal reactions which occur when acids and bases react in equivalent quantities, and in dilute aqueous solutions, are more closely examined it is found that the dibasic and tribasic acids fall into certain classes. Thomsen has especially examined this subject (*Th.* 1). The quantity of heat produced during the neutralisation of a dibasic acid is sometimes divisible into two exactly equal parts, according as one or two formula-weights of soda are allowed to react with one formula-weight of the acid. In other cases the thermal value of each stage of the total operation is different. Thus consider the following data:

$[H^2SiF^6Aq, NaOHAq] = 13{,}300$ $[H^2SO^4Aq, NaOHAq] = 14{,}750.$

$[H^2SiF^6Aq, 2NaOHAq] = 2 \times 13{,}300$ $[H^2SO^4Aq, 2NaOHAq] = (2 \times 14{,}750) + 1{,}900.$

$[H^2SO^3Aq, NaOHAq] = 15{,}850$

$[H^2SO^3Aq, 2NaOHAq] = (2 \times 15{,}850) - 2{,}750.$

Each of these three acids represents a group.

Thomsen divides the dibasic acids examined by him into three groups according as the thermal value of the action of the second formula-weight of soda is (1) equal to, (2) greater than, or (3) smaller than, the value of the action of the first formula-weight.

The data are presented in the following table:—

GROUP I.

Heat produced in action of NaOH	Acid H_2SiF_6	H_2PtCl_6
1st formula-weight	13,300	13,600
2nd " "	13,300	13,600

GROUP II.

	H_2SO_4	H_2SeO_4	$H_2C_2O_4$	$H_2C_4H_4O_6$
1st " "	14,750	14,750	13,850	12,450
2nd " "	16,650	15,650	14,450	12,850

GROUP III.

	H_2SO_3	H_2SeO_3	H_2CO_3	$H_2B_2O_4$
1st " "	15,850	14,750	11,000	11,100
2nd " "	13,100	12,250	9,150	8,900

	H_2CrO_4	H_2PHO_3	$C_2H_4(CO_2H)_2$
1st " "	13,150	14,850	12,400
2nd " "	11,550	13,600	11,750

The tribasic acids examined by Thomsen may also be classified according as the thermal value of the action of the second formula-weight of soda is greater or smaller than that of the first, and the value of the action of the third formula-weight is greater or smaller than that of the second. The data are as follows:—

GROUP I.

Heat produced in action of NaOH	Acid $H_3C_6H_3O_6$ (Aconitic Acid)	$H_3C_6H_5O_7$ (Citric Acid)
1st formula-weight	12,850	12,650
2nd " "	12,950	12,800
3rd " "	13,350	13,550

GROUP II.

Heat produced in action of NaOH	Acid H_3AsO_4	H_3PO_4
1st formula-weight	15,000	14,850
2nd " "	12,600	12,250
3rd " "	8,350	6,950

Group I. of the tribasic acids corresponds to Group II. of the dibasic, and Group II. of the tribasic, to Group III. of the dibasic, acids.

Thomsen suggests that this classification of dibasic and tribasic acids may be summarised in the following typical formulæ:—

DIBASIC ACIDS.

Acid of Group I.	Typical formula	RH_2	*e.g.* $SiF_6.H_2$;
Acid of Group II.	"	$R(OH)_2$	*e.g.* $SO_2(OH)_2$;
Acid of Group III.	"	$R(OH)H$	*e.g.* $SO_2(OH)H$.

TRIBASIC ACIDS.

Acid of Group I.	Typical formula	$R(OH)_3$	*e.g.* $C_6H_5O_4(OH)_3$;
Acid of Group II.	Typical formula	$HR(OH)H$	*e.g.* $HPO_2(OH)H$.

As regards dibasic acids; in the case of every acid examined by Thomsen, except two, the thermal value of the action of the first quantity of soda added is different from that of the second, equal, quantity of soda. The first of the typical formulæ suggested by Thomsen for the three classes of dibasic acids is probably to be assigned to H_2PtCl_6 and H_2SiF_6 only. Why should the formula $R(OH)_2$ rather than $R(OH)H$ be assigned to the acids of Group II.? The formula $R(OH)H$ would indicate the easy separation of the acids into anhydride (R) and water (OHH). But the acids placed in Group III. are, as a class, more easily separable into anhydride and water than those placed in Group II. If the differences between the thermal values of the first and second quantities of soda acting on the acids of Group III. are tabulated we have this result: $H_2SO_3 = 2,750$; $H_2SeO_3 = 2,500$; $H_2CO_3 = 1,850$; $H_2B_2O_4 = 2,200$; $H_2CrO_4 = 1,600$; $H_2PHO_3 = 1,250$; $C_2H_4(CO_2H)_2 = 650$. These differences vary from 9·5 (H_2SO_3) to 2·7 ($C_2H_4(CO_2H)_2$) per cent. of the total heat of neutralisation. We have good evidence in support of the statement that succinic acid is a dihydroxyl compound; therefore, although it occurs in Thomsen's third group, we must place it with those acids the typical formula of which is $R(OH)_2$, *i.e.* with the acids of Group II. The other acids of Group III. are fairly easily separable into anhydride and water. The formula $CO_2(OH)H$ for carbonic acid is to some extent confirmed by the fact that the higher homologues of this acid although dihydric are distinctly monobasic. If the differences between the thermal values of the first and second quantities of soda acting on the acids of Group II. are tabulated we have this result: $H_2SO_4 = 1,900$; $H_2SeO_4 = 900$; $H_2C_2O_4 = 600$; $H_2H_4C_4O_6 = 400$. These differences vary from 6 (H_2SO_4) to 1·5 ($H_2H_4C_4O_6$) per cent. of the total heat of neutralisation. The differences in the case of acids of Group III. are considerably larger than these. When the difference between the thermal values under consideration is small, and, as a rule, the value of the second quantity of soda is greater than that of the first, Thomsen regards the acid as, generally speaking, belonging to the type $R(OH)_2$; when the difference in question is large and the value of the second quantity of soda is, as a rule, smaller than that of the first, the acid is regarded as belonging to the type $R(OH)H$.

These thermal investigations made by Thomsen point to the performance of definite functions by the different hydrogen atoms in the chemically reacting unit, or group of atoms, of many polybasic acids. Although the reacting unit of a tribasic acid contains three atoms of hydrogen all replaceable by metal under similar conditions, nevertheless the energy-change which accompanies any one of these replacements is often different from the energy-change which accompanies the other replacements; hence we seem justified in concluding that each of the replaceable atoms of hydrogen in these acids is related to the rest of the atoms, which with the specified atom make up the chemically reacting unit of the acid, in a way different from that wherein the other replaceable atoms of hydrogen are related to the rest of the atomic complex in question.

In such acids as H_2SO_3, H_3PO_4, &c., it is necessary to exhibit the differences of function of the different replaceable atoms of hydrogen by formulæ which represent some of these acids as containing one OH group, others as containing two OH groups, and others three OH groups; but acids are known the reactions of which

oblige us to say that they contain more than one OH group, and at the same time to assert that each of these groups plays a different part in the reactions of the acid. Thus, glycollic acid $CH_2OH.COOH$ is a monobasic acid; the heat of neutralisation of this acid is

$[CH^2OH.COOHAq, NaOHAq] = 13{,}600$

(De Forcrand, *C. R.* 96, 582); but the addition of a second equivalent of soda to the neutral salt is attended with the production of a small quantity of heat

$[CH^2OH.COONaAq, NaOHAq] = 4{,}200$

(*ib.*, *Bl.* [2] 40, 104). The disodium glycollate thus formed is, however, an easily decomposed compound. Another monobasic acid, glyoxylic, is known, having the composition $CH(OH)_2.COOH$; this acid forms a definite sodium salt, an aqueous solution of which reacts with soda with the production of nearly one-sixth the quantity of heat produced by the reaction of the first equivalent of soda on the acid. The data are these (De Forcrand, *C. R.* 101, 1495):—

$[CH(OH)^2.COOHAq, NaOHAq] = 13{,}230$;

$[CH(OH)^2.COONaAq, NaOHAq] = 2{,}000$.

Here we have a very distinct illustration of the connections between thermal changes and the modification in the nature of the reaction of a specified group of atoms produced by the relations of that group to the other atoms, or group of atoms, in the chemically reacting unit of an acid (*v.* further AFFINITY; especially pp. 74, 75).

M. M. P. M.

ACIDS, ORGANIC. The empirical formula of acetic acid $C_2H_4O_2$ has been expanded into the structural formula $CH_3CO.O.H$ by reason of the following considerations. One fourth of the hydrogen of acetic acid is displaceable by metals; hence we write $C_2H_3O_2.H$. By the action of PCl_5, acetic acid may be made to exchange the same quantity of hydrogen together with half its oxygen for chlorine, producing acetyl chloride, C_2H_3OCl: hence we write $C_2H_3O.OH$. In the electrolysis of potassium acetate, ethane and carbonic acid are produced at the positive pole, potassium being formed at the negative pole. This decomposition may be represented thus; $C_2H_3O_2K = K + CO_2 + CH_3$; but methyl, CH_3, is immediately polymerised, becoming ethane, C_2H_6. This experiment shows that half of the carbon in acetic acid is intimately connected with oxygen, the other half being connected especially with hydrogen: hence we write, finally, $CH_3.CO.O.H$.

Analogous reasoning applied to other organic acids, very frequently leads to a similar formula, *e.g.* in the case of succinic acid to the formula $C_2H_4(CO.O.H)_2$. The acid character of these bodies is undoubtedly connected with the group $CO.O.H$ or CO_2H called *carboxyl*, and it is easy to generalise and say that all organic acids that are free from sulphur, phosphorus, arsenic or silicon, contain carboxyl. Kekulé, therefore, considers that the basicity of an organic acid is determined solely by the number of carboxyls it contains. Such a conclusion can, however, only be maintained, by *defining* an organic acid as a substance containing carboxyl. If this definition be accepted, it follows of course that all organic acids do contain carboxyl. But if we wish to let experiment guide us, we must adopt some other definition, such as that an acid is a substance that contains hydrogen which can be displaced by metals with the formation of a metallic compound not decomposable by water. According to this definition, phenol, pyrogallic acid, nitro-ethane, and even the propargyl derivatives and perhaps acetylene, are acids. Compounds like sugar-lime are not necessarily salts, for the calcium need not have displaced any hydrogen in the sugar, but may have added itself in some way.

Sodic carbonate gives off CO_2 when mixed with solutions of strong acids; if we adopt effervescence with sodic carbonate as a test of acidity, we shall consider the compounds just mentioned to be neutral bodies, but the nitrophenols and barbituric acid will still be acids. In testing with sodic carbonate we assume that carbonic acid is the weakest of all acids; this is a mere convention, the fact being that there is no definite line of demarcation between acids and neutral bodies, the two series shading off imperceptibly into one another.

It will be noticed that the acidity of phenol is greatly increased by the introduction of nitroxyl. In general, the displaceable hydrogen in an acid must be directly and indirectly attached to strong chlorous (or electro-negative) elements or radicles, for it is the balance of affinities between these elements or radicles and the metal that produces the stability of the salt. In carboxylic salts one O directly, and CO indirectly, neutralise or balance the metal, say sodium, forming the stable group CO.O.Na.

In sodium nitro-phenol, $NO_2.C_6H_4.O.Na$, the sodium is balanced by O directly and by NO_2 indirectly. In sodium nitrate, $NO_2.O.Na$, the condition of the molecule is similar (*v.* also ACETO-ACETIC ACID, p. 22). Too many or too few chlorous groups weaken an acid, for the equilibrium of its salts is thereby destroyed. Thus aldehyde, $CH_3.CO.H$ is a neutral body, while hydric hypochlorite, $Cl.O.H$, is a weaker acid than $Cl.H$.

For purposes of classification, it is most convenient to arrange acids according to their structural formulæ. Compounds whose structural formulæ exhibit closed rings, each containing more than two atoms, are classed as *aromatic*, a term that is more particularly applied to the derivatives of benzene; all other organic compounds belong to the *fatty* series.

Carboxylic acids of each series may be arranged according to their formulæ and general characters as follows:

A. *Fatty Series.*

(*a.*) *Monocarboxylic acids*: α. **Mono-hydric**: Series I, $C_nH_{2n}O_2$ or Acetic Series; Series II, $C_nH_{2n-2}O_2$ or Acrylic Series; Series III, $C_nH_{2n-4}O_2$ or Propiolic Series; Series IV, $C_nH_{2n-6}O_2$, *e.g.* tri-ethenyl-butyric.—β. **Di-hydric**: Series I, $C_nH_{2n}O_3$ or Lactic Series; Series II, $C_nH_{2n-2}O_3$, *e.g.* Oxy-acrylic; Series III, $C_nH_{2n-4}O_3$, *e.g.* oxypentinoic.—γ. **Tri-hydric**: $C_nH_{2n}O_4$ or Glyceric Series. —δ. **Ketonic**: Series I, $C_nH_{2n-2}O_3$, *e.g.* aceto-acetic acid; Series II, $C_nH_{2n-4}O_3$, *e.g.* allyl-aceto-acetic acid; Series III, $C_nH_{2n-6}O_3$, *e.g.* di-allyl-aceto-acetic acid.—ε. **Di-ketonic**: $C_nH_{2n-4}O_4$, *e.g.* acetyl-aceto-acetic acid.

(*b.*) *Di-carboxylic acids*: α. **Di-hydric**: Series I, $C_nH_{2n-2}O_4$ or Oxalic Series;

Series II, $C_nH_{2n-4}O_4$, *e.g.* fumaric acid; Series III, $C_nH_{2n-6}O_4$, *e.g.* acetylene di-carboxylic acid; Series IV, $C_nH_{2n-8}O_4$, *e.g.* di-acetylene di-carboxylic acid.—β. Tri-hydric: Series I, $C_nH_{2n-2}O_5$, malic series; Series II, $C_nH_{2n-4}O_5$, *e.g.* oxy-itaconic acid. — γ. Tetra-hydric, $C_nH_{2n-2}O_6$, *e.g.* tartaric acid.—δ. Penta-hydric, $C_nH_{2n-2}O_7$, *e.g.* tri-oxy-adipic acid.—ε. Hexa-hydric, $C_nH_{2n-2}O_8$, *e.g.* saccharic acid.—ζ. Ketonic, $C_nH_{2n-4}O_5$, *e.g.* acetyl-succinic acid.—η. Di-ketonic, $C_nH_{2n-6}O_6$, *e.g.* di-acetyl-succinic acid.

(*c*) *Tri-carboxylic acids*: α. Tri-hydric: Series I, $C_nH_{2n-4}O_6$, *e.g.* tricarballylic acid; Series II, $C_nH_{2n-6}O_6$, *e.g.* aconitic acid.—β. Tetra-hydric: $C_nH_{2n-4}O_7$, *e.g.* citric acid.—γ. Penta-hydric: $C_nH_{2n-4}O_8$, *e.g.* desoxalic acid.—δ. Ketonic: $C_nH_{2n-6}O_7$, *e.g.* acetyl-tricarballylic acid.

(*d*) *Tetra-carboxylic acids*: α. Tetra-hydric $C_nH_{2-6}O_8$, *e.g.* ethane tetra-carboxylic acid.

B. *Aromatic Series.* It is obvious that when rings of atoms are introduced into the structural formulæ, the empirical formulæ become very complicated. We shall therefore not attempt fully to classify the aromatic acids. The most important series are as follows:

(*a.*) *Mono-carboxylic acids*, α. Mono-hydric: $C_nH_{2n-8}O_2$, *e.g.* benzoic acid; $C_nH_{2n-10}O_2$, *e.g.* cinnamic acid; $C_nH_{2n-12}O_2$, *e.g.* phenyl-propiolic acid; $C_nH_{2n-14}O_2$, *e.g.* naphthoic acid; $C_nH_{2n-16}O_2$, *e.g.* di-phenic acid; $C_nH_{2n-18}O_2$, *e.g.* phenyl-cinnamic acid; $C_nH_{2n-20}O_2$, *e.g.* anthracene carboxylic acid; $C_nH_{2n-24}O_2$, *e.g.* tri-phenyl-acetic acid.—β. Di-hydric: $C_nH_{2n-8}O_3$, *e.g.* salicylic acid; $C_nH_{2n-10}O_3$, *e.g.* coumaric acid.—γ. Tri-hydric: $C_nH_{2n-8}O_4$, *e.g.* protocatechuic acid, $C_nH_{2n-10}O_4$, *e.g.* oxy-coumaric acid.—δ. Tetra-hydric, $C_nH_{2n-8}O_5$, *e.g.* gallic acid.—ε. Ketonic: $C_nH_{2n-10}O_4$, *e.g.* oxy-acetophenone carboxylic acid.

(*b.*) *Di-carboxylic acids*: α. Di-hydric: $C_nH_{2n-8}O_4$, *e.g.* hydro-terephthalic acid; $C_nH_{2n-10}O_4$, *e.g.* phthalic acid.—β. tri-hydric: $C_nH_{2n-10}O_5$, *e.g.* oxy-phthalic acid.

The more complicated aromatic acids may be classified in a similar way. It will be seen that they are all poorer in hydrogen than the corresponding fatty acids.

Organic Acids in general.—*Occurrence*: In the vegetable kingdom, *e.g.* oxalic, malic, tartaric, benzoic, salicylic, cinnamic, veratric, gallic, and tannic acids. In animal juices and secretions, *e.g.* lactic, sarcolactic, uric, hippuric, glycocholic, and taurocholic acids. In decaying organised matter, *e.g.* acetic, butyric, valeric, amido-propionic, amido-hexoic, and glutamic acids.

Formation.—1. By decomposing products of the animal or vegetable kingdom by boiling with dilute acids, *e.g.* amido-acetic, aspartic and glutamic acids.—2. From fats and fatty oils by boiling with alkalis, *e.g.* stearic, palmitic, and oleic acids.—3. From resins by potash-fusion, *e.g.* *p*-oxy-benzoic and protocatechuic acids.—4. By boiling a variety of substances with dilute nitric acid (S.G. 1·2), *e.g.* oxalic and tartaric acids from sugar and other carbohydrates.—5. By oxidising aromatic hydrocarbons and other bodies with chromic mixture (2 pts. of $K_2Cr_2O_7$, 3 pts. of H_2SO_4 and 3 to 5 parts of water), *e.g.* benzoic and terephthalic acids.—6. By oxidation with $KMnO_4$, *e.g.* vanillic acid from coniferin, pyridine carboxylic acids from methyl-pyridines.—7. From nitriles by boiling with KOH, *e.g.* acetic and succinic acids. Unstable nitriles must be first converted into amides by cold conc. HCl, and the amides may then be turned into acids by boiling dilute HCl, *e.g.* pyruvic acid (Claisen). The nitriles may be prepared from alkyl chlorides or potassic alkyl sulphates by distilling with KCy or digesting with $HgCy_2$. No nitriles of the form $XYC(CN)_2$ are known (Claus), hence derivatives of malonic acid cannot be prepared in this way.—8. By the oxidation of primary alcohols: $X.CH_2.OH + O_2 = X.CO.OH + H_2O$. Secondary and tertiary alcohols can only produce acids with a less number of carbon atoms, *e.g.* $CH_3.CH(OH).CH_3 + 5O = CH_3CO_2H + CO_3H_2 + H_2O$.

Preparation.—The acids may be separated from insoluble neutral and alkaline substances by solution in aqueous potash; they may then be liberated by H_2SO_4 and purified by one of the following methods:

(*a.*) If they are volatile, they are distilled alone or with steam.

(*b.*) By conversion into a lead, barium, or silver salt and, if possible, purifying the salt by crystallisation. The lead salt is then decomposed by H_2S, the barium salt by the calculated quantity of H_2SO_4, and the silver salt either by H_2S or by the calculated quantity of HCl.

(*c.*) By acidifying and extracting with ether. A large number of acids are soluble in ether.

Reactions.—1. Organic acids may be converted into ethers in two principal ways: (*a.*) By distilling with an alcohol and dilute H_2SO_4. The reaction may be supposed to take place in two stages; the preparation of acetic ether may be thus represented:

$$EtOH + H_2SO_4 = EtHSO_4 + H_2O$$
$$EtHSO_4 + HOAc = EtOAc + H_2SO_4.$$

(*b.*) If an acid is non-volatile, it is dissolved in the alcohol and the liquid is saturated with HCl. After some hours the solution is poured into water and the ppd. ether distilled, if possible, *in vacuo*; the reactions may be thus represented:

$$EtOH + HCl = EtCl + H_2O$$
$$EtCl + HOAc = EtOAc + HCl.$$

It is not necessary that HCl or H_2SO_4 should be present in order that etherification may take place, for if equivalent quantities of an acid and an alcohol be left in contact or heated together for a sufficiently long time, from 64 to 74 p.c. will react upon each other, forming an ether. The rate at which the reaction takes place is greatest for acids of the formula $X.CH_2.CO_2H$, slower for so-called secondary acids, $XYCH.CO_2H$, and slowest for tertiary acids of the type $XYZ.C.CO_2H$, where X, Y and Z are alkyls (Menschutkin, *v.* CHEMICAL CHANGE).—2. Chlorides of phosphorus convert acids or their salts into acid chlorides of the form X.CO.Cl. These are usually soluble in ether, and are decomposed by water, more or less rapidly, into HCl and the acid X.CO.OH. Oxy-acids exchange not only their carboxylic hydroxyl for Cl, but also their other hydroxyls; but the chlorides so produced are not reconverted by water into the original acid but only into chloro-

acids; thus lactic acid, $CH_3.CH(OH).CO_2H$, is converted by PCl_5 into lactyl chloride, $CH_3.CHCl.COCl$, whence water reproduces chloropropionic acid, $CH_3.CHCl.CO_2H$. The chlorides act upon dry nitrates of the heavy metals (Ag, Pb, Cu, Zn, and Hg) producing anhydrides, *e.g.*:

$$2Ph.CO.Cl + Pb(NO_3)_2 = (Ph.CO)_2O + PbCl_2 + N_2O_4 + O$$

(Lachowicz, *B.* 18, 2990).—3. Amides are formed by the action of NH_3 either upon the chlorides: $X.COCl + 2NH_3 = X.CO.NH_2 + NH_4Cl$, or ethers: $X.CO.OEt + NH_3 = X.CO.NH_2 + HOEt$. The amides are usually crystalline substances, and their melting-points form important means of recognising the various acids.—4. Acetyl chloride converts acids into anhydrides (*v.* ACETYL CHLORIDE).—5. $COCl_2$ converts salts into anhydrides.—6. By heating with CaO or BaO, or sometimes by heating alone, CO_2 can be eliminated from the carboxyls.—7. Dry distillation of calcium or barium salts usually produces ketones (*q. v.*).—8. Distillation of calcium salts with calcium formate usually produces aldehydes (*q. v.*).

Salts.—Salts are formed by neutralising the acids with metallic oxides or carbonates. They can be conveniently obtained by the addition of metallic sulphates or soluble carbonates to a solution of the barium salt of the acid, or of soluble chlorides to the solution of the silver salt. Sodium, added to ethereal or alcoholic solutions of oxy-acids, displaces not only carboxylic but also hydroxylic hydrogen. The compounds so produced are, in many cases, partly decomposed by water, the sodium that has displaced alcoholic hydroxyl being turned out again, *e.g.* $CH_3.CH(ONa).CO_2Na + H_2O = CH_3.CH(OH).CO_2Na + NaOH$. The silver salt is usually the least soluble, and is frequently used in determining the molecular weight of an acid; for when the basicity of an acid is known the molecular weight can be deduced from the percentage of silver left after strongly heating the salt. Silver salts seldom contain water of crystallisation.

Acetic Series $C_nH_{2n}O_2$. *Nomenclature.*—The following names are employed in this dictionary, the numbers denoting the value of n: **1.** formic acid, **2.** acetic acid, **3.** propionic acid, **4.** butyric acid, **5.** valeric acid, **6.** hexoic acid = caproic acid, **7.** heptoic acid = œnanthic acid, **8.** octoic acid = caprilic acid, **9.** ennoic acid = nonylic acid = pelargonic acid, **10.** decoic acid = capric acid, **11.** hendecoic acid = undecylic acid, **12.** dodecoic acid = lauric acid, **13.** tridecoic acid, **14.** tetradecoic = myristic acid, **15.** pentadecoic acid, **16.** palmitic acid = hexadecoic acid, **17.** heptadecoic acid, **18.** stearic acid = octodecoic, **19.** enendecoic acid = arachic acid, **20.** behenic acid = icosoic acid.

Formation.—Besides the general methods described above, the following may be noticed:—**1.** The action of CO_2 upon sodium alkyls, *e.g.* $NaC_2H_5 + CO_2 = C_2H_5.CO_2Na$. This gives one method for preparing fatty acids from compounds containing a fewer number of atoms of carbon in the molecule; another method depends upon the saponification of alkyl cyanides (*v. supra*).—2. The action of strong KOH upon alkylated aceto-acetic ethers (*q. v.*).—3. The distillation of alkyl-malonic acids: $XYC(CO_2H)_2 = XYCH.CO_2H + CO_2$, where X and Y may be alkyls or hydrogen. Other di-basic acids are decomposed in a similar way when their solutions are mixed with uranium nitrate solution and exposed to sunlight.—5. By heating sodium alcoholates with CO gas: $NaOEt + CO = EtCO_2Na$.—6. By reducing oxy-acids by heating with HI.—7. By reducing unsaturated acids by HI or sodium-amalgam.

Reactions.—1. Dry distillation of salts of the alkaline earths or alkalis produces ketones: *e.g.*

$$Ca(O.CO.Me)_2 = CaCO_3 + COMe_2.$$

2. Distillation of a mixture of such salts of two acids produces mixed ketones:

$$KO.CO.Me + KO.CO.Et = K_2CO_3 + Me.CO.Et.$$

If one of the salts be a formate the product is an aldehyde:

$$KO.CO.Me + KO.CO.H = K_2CO_3 + Me.CO.H.$$

3. Distillation of a salt of a fatty acid with an alkaline hydrate produces a hydrocarbon:

$$KO.CO.Me + KO.H = K_2CO_3 + MeH.$$

4. Distillation of the alkaline saltsw ith As_2O_3 gives organic compounds containing ARSENIC (*q.v.*)
5. Electrolysis gives saturated hydrocarbons:

$$2C_nH_{2n+1}.CO_2K = K_2 + 2CO_2 + C_{2n}H_{4n+2}.$$

6. Chlorine and bromine act by substitution, not by addition.—7. Distillation in a current of steam of the mixture of stearic, palmitic, and oleic acids got from fat slightly decomposes them, forming all acids of the series from formic to octoic (Cahours a. Demarçay, *C. R.* 90, 156).

Synthesis.—The acids of the acetic series may be built up in the following way:—(*a*) NaMe is converted into $NaCO_2Me$, or sodic acetate, by CO_2 (Wanklyn).—(*b*) Sodic acetate is converted into ethyl alcohol in one of three ways: *α*. It is converted by $POCl_3$ into Ac_2O, and this is reduced by sodium-amalgam (Linnemann).—*β*. Ammonic acetate is prepared, and is converted by P_2O_5 into acetonitrile: $NH_4CO_2Me = 2H_2O + NCMe$; the nitrile is then reduced by Zn and H_2SO_4 (Mendius) to an amine: $NCMe + 2H_2 = H_2N.CH_2Me$, which is converted by nitrous acid into an alcohol: $H_2N.CH_2Me + HNO_2 = HO.CH_2Me + N_2 + H_2O$. This last reaction is, however, accompanied by an intra-molecular change in the case of all the amines except ethylamine and methylamine; as a result of this change *n*-propylamine gives rise to secondary as well as *n*-propyl alcohol.—*γ*. The sodic acetate is mixed with sodic formate and distilled; the aldehyde thus got is reduced to alcohol by sodium-amalgam (Lieben a. Rossi), or the oxim of the aldehyde is reduced to an amine which is then treated with nitrous acid.—(*c*) Ethyl alcohol so prepared can now be turned into ethyl iodide, zinc ethide, and sodium ethide, successively.

A repetition of processes (*a*), (*b*) and (*c*) upon NaEt will produce sodic propionate, propyl alcohol, and sodic propide successively, and so we can build up the series of fatty acids.

Instead of using the sodium alkyls, it is more convenient to use alkyl cyanides; the process is then: (*a*) convert methyl alcohol into methyl cyanide, and this, by saponification, into acetic acid; (*b*) convert acetic acid into ethyl alcohol by one of the three processes, *α*, *β*, or *γ*, just mentioned; (*c*) convert ethyl alcohol into ethyl cyanide, and proceed as before to prepare propionic acid, propyl alcohol &c. The acids of the acetic series may also be prepared synthetically with the aid of aceto-acetic ether (p. 22) or

of malonic ether (*q. v.*). In this way any acid of the form $CHXY.CO_2H$, where X and Y are alkyls, can be prepared.

The descent of the acetic series may be effected by distilling each acid with soda-lime, whereby a hydrocarbon containing one atom of carbon less is got; this hydrocarbon is converted by chlorine into an alkyl chloride, whence by successive treatment with AgOAc and KOH an alcohol may be formed.

The descent may also be effected by converting the acid into an amide, mixing this with bromine and pouring the mixture into a 10 per cent. solution of NaOH. An amine, a nitrile, and a derivative of urea are then formed, the amine and the nitrile contain one atom of carbon less than the amide. The amine may be turned into an alcohol by nitrous acid, and then oxidised to an acid; while the nitrile gives the acid on mere saponification. The amides containing at least 8 carbon atoms yield large quantities of nitrile, while the lower amides produce chiefly amine (Hofmann, *B.* 17, 1408). The descent through nitrile from ennoic to octoic acid may be thus represented:

$$C_8H_{17}CONH_2 + 3Br_2 + 8NaOH =$$
$$C_8H_{15}CN + 6NaBr + Na_2CO_3 + 6H_2O.$$
$$C_7H_{15}CN + KOH + H_2O = C_7H_{15}CO_2K + NH_3.$$

Melting Points.—While the boiling points of the acetic series of acids gradually rise with each increment of CH_2, the melting-points of those acids that contain an odd number of atoms of carbon appear to be lower than those of the acids that contain one atom of carbon less:

caprilic	[16·5°]	pelargonic	[12·5°]
capric	[30°]	hendecoic	[28·5°]
lauric	[43°]	tridecoic	[40·5°]
myristic	[53·8°]	pentadecoic	[51°]
palmitic	[62°]	margaric	[59·9°]
stearic	[69°]	enendecoic	[59·9°]
arachic	[75°]	medullic (?)	[72·5°]

Isomerism among the fatty acids will be discussed under CLASSIFICATION (*v.* also ISOMERISM).

Separation of two volatile acids.—Divide the acid into two equal parts, neutralise one with potash, add the other and distil. The most volatile acid will pass over in preference to the other; and if it constitutes more than half the entire mixture, the distillate will consist solely of this acid. If, however, the less volatile acid be in excess, the residue will consist of its potassium salt in a pure state. The operation is repeated upon whichever portion is still a mixture. Acetic acid is an exception to the rule, for although it be the more volatile acid, it will remain behind as acid potassium acetate (Liebig, *A.* 71, 355). If the distillation be performed in aqueous solution in a current of steam, the acid of highest molecular weight goes over first (Hecht, *A.* 209, 319).

Separation of fixed acids.—An alcoholic solution of the mixture of acids is fractionally precipitated by a conc. aqueous solution of magnesium or barium acetate or by an alcoholic solution of lead acetate. In the series of pps. so got, the first contains the acid of highest molecular weight and the last the acid of lowest molecular weight. Each fraction is decomposed by boiling dilute HCl and the melting-point taken. If a series of consecutive fractions contains acids of identical melting-point that acid may be considered pure, otherwise the process must be repeated upon each fraction (Heintz, *J. pr.* 66, 1; *A.* 92, 295).

Acrylic Series $C_nH_{2n-2}O_2$. *Nomenclature.*—n = 3, acrylic; 4, crotonic; 5, angelic; 6, hexenoic; 7, heptenoic; 8, octenoic = suberonic; 9, ennenoic; 10, decenoic = campholic; 11, hendecenoic = undecylenic; 12, dodecenoic; 14, tetradecenoic; 15, pentadecenoic = cimicic; 16, hexadecenoic = hypogæic; 18, oleic = octodecenoic; 19, doeglic = enendecenoic; 22, erucic and brassic acids.

Occurrence.—As compound ethers in fats and oils, *e.g.* oleic acid.

Formation.—1. From β-, and sometimes from α-, bromo- or iodo- derivatives of the acetic series by boiling with alkalis or Ag_2O:

$$CH_2I.CH_2.CO_2K + KOH =$$
$$CH_2:CH.CO_2K + KI + H_2O.$$

2. From β-oxy-acids, by distillation:

$$CH_2OH.CH_2.CO_2H = H_2O + CH_2:CH.CO_2H.$$

3. From certain β-oxy-ethers by PCl_3:

$$3CMe_2OH.CO_2Et + 2PCl_3 =$$
$$3CMe_2Cl.CO_2Et + P_2O_3 + 3HCl$$
$$CMe_2Cl.CO_2Et = CH_2:CMe.CO_2Et + HCl$$

(Frankland a. Duppa, *C. J.* [2] 3, 133). Similarly $Me_2C(OH).CH_2.CO_2Et$ gives $Me_2C:CH.CO_2Et$.—4. From derivatives of aceto-acetic or malonic ethers containing allyl, ethylene, &c.—5. By Perkin's reaction, by heating aldehydes, $C_nH_{2n}O$, with sodic acetate and Ac_2O (*v.* ALDEHYDES).

Properties.—As in the acetic series, the lower members of the acrylic series are volatile liquids miscible with water. Solubility and specific gravity diminish as molecular weight and boiling point increase. The higher members are non-volatile and insoluble in water.

Reactions.—1. The acids of this series contain the group C:C and consequently combine directly with bromine and chlorine, usually with HBr or HI in conc. solution, and frequently with H_2, the latter combination is effected either by action of sodium amalgam on a solution in water or alcohol or by heating with conc. HI.—2. Fusion with potash produces two acids, one of which is almost always acetic acid. The molecular formula is split up in the middle of the group C:C, *e.g.*:

$$CH_3.CH:CH.CO_2H + 2KOH =$$
$$CH_3CO_2K + H_2CH.CO_2K + H_2.$$

3. Boiled dilute with H_2SO_4, they often change into the lactone of saturated oxy-acids: thus hydro-sorbic acid, $CH_3.CH:CH.CH_2.CH_2.CO_2H$, changes into oxy-hexo-lactone,

$$CH_3.CH_2.\underline{CH.CH_2.CH_2.CO.O}$$

4. Many of the higher members are polymerised by nitrous acid.

Series $C_nH_{2n-4}O_2$. *Nomenclature.*—n = 3. Propiolic; 4, tetrolic; 5, pentinoic; 6, hexinoic = sorbic; 7, heptinoic = benzoleic; 8, octinoic = di-allyl-acetic; 9, lauronolic = enninoic; 10, camphic = decinoic; 11, hendecinoic = undecolic; 14, myristolic = tetradecinoic; 15, pentadecinoic; 16, palmitolic = hexadecinoic; 17, elæomargaric = heptadecinoic; 18, stearolic = octodecinoic; 22, behenolic.

Formation.—From di-brominated (or di-chlorinated) acids of the acetic series, or mono-

brominated acids of the acrylic series by treatment with alcoholic KOH.

Reactions.—Combine with Br_2 or with Br_4, also with HBr or 2HBr, and with H_2 and sometimes with H_4.

Lactic Series $C_nH_{2n}O_3$. *Nomenclature.*—n = 2, Glycollic; 3, lactic and hydracrylic; 4, oxybutyric; 5, oxy-valeric; 6, oxy-hexoic &c.—*oxy* being prefixed to the names used in the acetic series.

Formation.—1. By the general methods: thus (7) by saponification of oxy-nitriles, (8) by oxidation of glycols.—2. From bromo-, chloro- or iodo- derivatives of the acetic series by displacing the halogen by hydroxyl: (*a*) by boiling with much water, (*b*) by moist Ag_2O, or (*c*) by KOHAq.—3. From amido-acids by nitrous acid. 4. From aldehydes or ketones by addition of HCN followed by saponification of the resulting cyanhydrin by HCl:

$$CH_3.CHO + HCN = CH_3.CH(OH).CN$$
$$CH_3.CH(OH).CN + HCl + 2H_2O = CH_3.CH(OH).CO_2H + NH_4Cl.$$

5. By oxidation of acids containing methenyl:

$$(CH_3)_2CH.CO_2H + O = (CH_3)_2C(OH).CO_2H.$$

6. By action of zinc alkyls on oxalic ethers:

$$CO_2Et.CO_2Et + 2ZnEt_2 = CO_2Et.CEt_2.OZnEt + EtZnOEt,$$
$$CO_2Et.CEt_2.OZnEt + 2H_2O = CO_2Et.CEt_2.OH + Zn(OH)_2 + C_2H_6.$$

7. By reduction of ketonic acids.

Reactions.—The action of PCl_5 and of Na, and the characters of the resulting compounds have been discussed above. The oxy-acids act as half alcohol and half acid. Thus they form two kinds of monoethylic ethers, one of the form $R''(OH).CO_2Et$, the other of the form $R''(OEt).CO_2H$. The ethers $R''(OH).CO_2Et$ possess all the characters of an ethyl salt of an acid. Thus they may be prepared in the usual way from the acid, alcohol, and HCl; they may be saponified easily by alkalis; they are converted by ammonia into amides $R''(OH).CONH_2$; they are neutral to litmus. The ethers of the form $R''(OEt).CO_2H$ can be prepared by saponifying the diethylic ethers $R''(OEt).CO_2Et$ and these are got from $R''Cl.CO_2Et$ by action of NaOEt. The ethers $R''(OEt).CO_2H$ cannot be saponified by alkalis; are only converted into ammonium salts, $R''(OEt).CO_2NH_4$, by ammonia; and are acid to litmus.

α-oxy-acids are split up by boiling conc. HCl into formic acid and aldehydes:

$$CH_3.CH(OH).CO_2H = CH_3.CHO + HCO_2H.$$

β-oxy-acids boiled with conc. HCl give H_2O and an acid of the acrylic series:

$$CH_2OH.CH_2.CO_2H = CH_2{:}CH.CO_2H + H_2O.$$

γ-oxy-acids split up, when their solution is warmed, into water and lactones (*q. v.*).

$$CH_3.CH(OH).CH_2.CH_2.CO_2H = \underline{CH_3.CH.CH_2.CH_2.CO.O} + H_2O$$

On dry distillation, the *α*-oxy-acids of the form $R'.CH(OH).CO_2H$ produce lactides, or compound ethers of the form $R'.CH{<}{}^{O.CO}_{CO.O}{>}CH.R'$. The *β*-oxy-acids are converted by dry distillation into unsaturated acids:

$$R'.CH(OH).CH_2.CO_2H = R'.CH{:}CH.CO_2H + H_2O,$$

or into an aldehyde and an acid:

$$CH_3.CH(OH).CRR'.CO_2H = CH_3.CHO + HCRR'.CO_2H.$$

Ketonic acids. Carboxylic acids represented by formulæ in which carbonyl is united to two atoms of carbon. The preparation and properties of the ketonic acids got by displacing one or two atoms of hydrogen in aceto-acetic acid by hydrocarbon radicles are described under ACETO-ACETIC ACID. Homologues of aceto-acetic acid in which carbonyl and carboxyl are not both united to the same atom of carbon are described as alkoyl-derivatives of fatty acids; thus, $CH_3.CH_2.CO.CH_2.CH_2.CO_2H$ is described as PROPIONYL-PROPIONIC ACID.

Ketonic acids containing two carboxyls are described as derivatives of di-basic acids, thus $CH_3.CO.CH(CO_2H).CH_2.CO_2H$ is described as acetyl-succinic acid.

Ketonic acids of the form $R'CO.CO_2H$ can be prepared from cyanides of the form $R'.CO.CN$, and also, in the aromatic series, by the action of $HgPh_2$ &c., on $ClCO.CO_2Et$.

Di-basic acids, $C_nH_{2n-2}O_4$.

Formation.—1. By oxidation of the corresponding glycols.—2. By boiling the cyanides of alkylenes with potash. Alkylidene cyanides do not exist (Claus).—3. By saponification of cyano-acids, $C_nH_{2n-1}CyO_2$.—4. By reduction of unsaturated di-basic acids.—5. By action of reduced silver upon iodo-acids (*e.g.* formation of adipic from iodo-propionic acid).—6. By oxidation of fats, fatty acids, ketonic acids, unsaturated acids and many other bodies.—7. By reducing polyhydric di-carboxylic acids by HI, *e.g.* tartaric acid to succinic.—8. From aceto-acetic ethers by acting with NaOEt and the ethyl salt of a chloro- or bromo-acid, and saponifying the product with conc. KOH (*v.* ACETYL-SUCCINIC ETHER).—9. From sodio-malonic ether and alkyl iodides:

$$CHNa.(CO_2Et)_2 + IR = CHR(CO_2Et)_2 + NaI.$$

The product still contains hydrogen displaceable by sodium: $CHR(CO_2Et)_2 + Na = CNaR(CO_2Et)_2 + H$ whence alkyl iodides form di-alkylated malonic ether:

$$CNaR(CO_2Et)_2 + R'I = CR'R(CO_2Et)_2 + NaI$$

(*v.* MALONIC ACID).

Properties.—Solid and not volatile. Frequently produce anhydrides when heated. Malonic acid and its derivatives are split up by heat into CO_2 and acids of the acetic series. In the oxalic series the acids containing an even number of carbon atoms in the molecule have higher melting-points, and lower solubility in water than the acids with an uneven number of carbon atoms (Baeyer, *B.* 10, 1286; Henry, *C.R.* 99, 1157; 100, 60).

For the characters of the homologues of benzoic and salicylic acids see AROMATIC SERIES. See also AMIDO-, BROMO-, CHLORO-, IODO- and NITRO-ACIDS, and SULPHONIC ACIDS.

ACONIC ACID

$$C_5H_4O_4 \text{ i.e. } CO_2H.CH_2.C{<}{}^{CO}_{CH}{>}O$$

M. w. 128. [163°-164°]. S. 17·8 at 15°. Formed by boiling itadibromopyrotartaric acid with a caustic alkali, $C_5H_6Br_2O_4 = 2HBr + C_5H_4O_4$ (Kekulé, *A. Suppl.* 1, 338), or with water (10 pts.) (Beer, *A.* 216, 92). In like manner from bromoitaconic acid, $C_5H_5BrO_4$ (Swarts, *J.* 1873, 584). To prepare it, a solution of itadibromopyrotartaric acid neutral-

ised with soda is heated to the boiling point, then gradually mixed with more soda till it contains 3 mol. NaOH to 1 mol. of the acid. On evaporating the solution, sodium aconate crystallises out and aconic acid may be obtained from it by decomposition with sulphuric acid and agitation with ether (Meilly, *A.* 171, 153).

Separates from water in rhombic crystals; from ether in elongated laminæ (M.).

Reactions.—1. Decomposed slowly by boiling water, forming a brown syrup.—2. Does not combine with bromine.—3. Unites with HCl and HBr forming chloro- and bromo-itaconic acids (Swarts).—4. Reduced by Sn or Zn to itaconic acid.—5. Boiling baryta produces formic, succinic and oxy-itaconic acids:

$$C_5H_4O_4 + 2H_2O = CH_2O_2 + C_4H_6O_4 \text{ and}$$
$$C_5H_4O_4 + H_2O = C_5H_6O_5.$$

Salts.—BaA'_2: v. sol. water, ppd. by alcohol; crystallises from hot alcohol in shining prisms; gives off $2\frac{1}{2}$ aq. at 150°.—$CuA'_2$4aq: blue prisms. —AgA': sparingly soluble laminæ. NaA'3aq: efflorescent triclinic crystals: $a : b : c = \cdot538 : 1 : \cdot699$; $\alpha = 103°6'$, $\beta = 101° 27'$, $\gamma = 84° 49'$. Got by boiling ita-di-bromo-pyrotartaric acid with the calculated quantity of aqueous Na_2CO_3. It is decomposed by long boiling with water (B.).—$ZnA'_2$8aq: large shining crystals, melting below 100° in their water of crystallisation.

Methyl Ether. MeA' [85°]. From AgA' and MeI. Long thin prisms, v. sol. ether, m. sol. alcohol, sl. sol. water. H. W.

ACONITANILIC ACID *v.* ANILINE.

ACONITE ALKALOIDS. —1. **Aconitine.** $C_{33}H_{43}NO_{12}$.[183° cor.]. S. ·13; S (benzene or chloroform) 18; S. (ether) 1·56; S. (alcohol) 2·7; S. (petroleum) ·036 (Jürgens, *Ar. Ph.* [3] 24, 127).

Occurrence.—In the root of monk's-hood, *Aconitum Napellus* (Geiger a. Hesse, *A.* 7, 276; Planta, *A.* 74, 257).

Preparation.—The ground root is exhausted with alcohol containing tartaric acid; the concentrated extract, after exposure to the air in shallow dishes to remove the last traces of alcohol, is mixed with water; the aqueous solution is filtered to separate resin, the last portions of which are removed by agitation with light petroleum, and then precipitated with potassium carbonate; the precipitate, consisting chiefly of aconitine, is dissolved in ether, which leaves behind a small quantity of humous substance; the solution is mixed with aqueous tartaric acid and precipitated with sodium carbonate; the precipitate is dissolved in ether; and the etheric solution left to evaporate. The residue consists of nearly pure aconitine, which may be further purified by converting it into hydrobromide, decomposing this salt, after recrystallisation, with sodium carbonate, and finally recrystallising the precipitate from ether (Duquesnel, *C. R.* 73, 207; Wright, *C. J.* 31, 150).

Properties.—Crystallises in rhombic or hexagonal plates. Soluble in alcohol, ether, benzene, very soluble in chloroform, insoluble in light petroleum. Extremely poisonous; the minutest particles, inhaled or blown into the eye produce excessive irritation (W., *C. J.* 31, 154; Wright a. Luff, *C. J.* 33, 325). Lævogyrate (D.).

Reactions.—Slightly alkaline; forms well-crystallised salts. Resolved by heating with alcoholic KOH into benzoic acid and **aconine**:

$C_{33}H_{43}NO_{12} + H_2O = C_7H_6O_2 + C_{26}H_{39}NO_{11}$;—partly also in the same manner by dilute mineral acids, but another portion is at the same time resolved into water and **apoaconitine.** Acetic and benzoic anhydrides convert it into **acetyl** and **benzoyl-apoaconitine** (W. a. L.). The *hydrobromide* forms crystals containing $C_{33}H_{43}NO_{12},HBr,2\frac{1}{2}H_2O$; the *hydrochloride* $C_{33}H_{43}NO_{12},HCl,3H_2O$, forms with auric chloride the salt $C_{33}H_{43}NO_{12},HCl,AuCl_3$, which separates in pale yellow amorphous flakes very slightly soluble in water (W.).

Apoaconitine $C_{33}H_{41}NO_{11}$.[186°].—Formed, together with benzoic acid and aconine, by prolonged boiling of aconitine with sulphuric acid (5 p.c.) or with a saturated solution of tartaric acid. The benzoic acid which separates is dissolved out by ether and the apoaconitine is precipitated by sodium carbonate, while the aconine remains dissolved. Crystals soluble in ether. As poisonous as aconitine. The *hydrobromide* $C_{33}H_{41}NO_{11},HBr.2\frac{1}{2}H_2O$ is crystalline (W. a. L.).

Acetyl-apoaconitine $C_{33}H_{40}AcNO_{11}$.[181°]. Soluble in ether, separates therefrom in small crystals. Dissolves easily in acids, forming amorphous salts (W. a. L.). *Benzoylapoaconitine* $C_{40}H_{45}NO_{12} = C_{33}H_{40}BzO_{11}$, obtained by heating aconitine or aconine with Bz_2O, is indistinctly crystalline, softens at about 130°, forms amorphous salts. Nitrate nearly insoluble (W. a. L.).

Aconine $C_{26}H_{39}NO_{11}$ [130°]. Formed, together with benzoic acid, by the action of aqueous alkalis, or more completely by that of alcoholic NaOH, on aconitine (*v. sup.*). V. sol. water, alcohol, alkalis and chloroform, insol. ether. Amorphous. Reduces gold and silver salts at ord. temp., Fehling's solution when heated.

Salts.—$3C_{26}H_{39}NO_{11},2HCl$ and $B'_7H_2SO_4$ are amorphous and probably only mixtures. $B'HClAuCl_3$ is a yellow flocculent pp. $B'HHgI_3$ is a white flocculent pp. (W. a. L.).

Apoaconine, $C_{26}H_{37}NO_{10}$ is formed by heating the hydrochloride of aconine at 140°. $C_{26}H_{37}NO_{10}HCl$ is amorphous, soluble in water, precipitated by alkalis.

2. **Picroaconitine** $C_{31}H_{45}N_{10}$.—Found by T. B. Groves in a commercial aconite root, supposed to be that of *A. Napellus.* Amorphous varnish, having a bitter taste, but not producing any prickly sensation on the tongue. Not poisonous. Does not melt at 100°. Salts crystallise well. The *hydrochloride* contains $C_{31}H_{45}NO_{10}HCl,\frac{3}{2}H_2O$. The *gold salt* $B'HClAuCl_3$, is a canary-yellow amorphous precipitate very slightly soluble in water (W.).

Picroaconine $C_{24}H_{41}NO_9$. Formed, together with benzoic acid, by the action of alcoholic KOH on picroaconitine. Closely resembles aconine. Forms $C_{24}H_{41}NO_9HIHgI_2$ (W. a. L.).

3. **Pseudaconitine** $C_{36}H_{49}NO_{12}$ [104°-105°]. The chief basic constituent of the root of *Aconitum ferox*, from which it is obtained by exhausting with alcohol and sulphuric acid (0·05 p.c. of the weight of the alcohol), or with methylated spirit (640 c.c.) containing a little HClAq (1 c.c.), leaving the alcohol to evaporate, precipitating the remaining solution with ammonia, dissolving the precipitate in ether, and evaporating. The crystals which separate are purified by

recrystallisation from a mixture of ether and light petroleum, or by means of the nitrate.

Properties.—More soluble in alcohol and ether than aconitine; crystallises in transparent needles and sandy crystals; remains syrupy after rapid evaporation. The air-dried base contains 1 mol. H_2O, given off at 80° in a stream of air, more quickly at 100°; decomposes, with separation of water at 130°-140°. Decomposed by alcoholic soda at 100° into pseudaconine and veratric acid:

$$C_{36}H_{49}NO_{12} + H_2O = C_{27}H_{41}NO_9 + C_9H_{10}O_4$$

at 140° into veratric acid and apopseudaconine, $C_{27}H_{39}NO_8$. By mineral acids it is resolved into water and apopseudaconitine; with acetic acid it forms acetylapopseudaconitine. Salts mostly amorphous; nitrate $C_{36}H_{49}NO_{12}\,NO_3H\,3H_2O$, crystalline. $B'HClAuCl_3$ crystallises from alcohol in small needles, slightly soluble in cold alcohol. $B'HIHgI_2$ is an amorphous flocculent pp. (W. a. L.)

Apopseudaconitine $C_{36}H_{47}NO_{11}$ [103°]. Formed, together with pseudaconine and veratric acid, by heating pseudaconitine with dilute mineral acids, or with veratric acid alone when pseudaconitine is heated at 100° with a saturated aqueous solution of tartaric acid. Crystallises from ether in the same forms as pseudaconitine. The *nitrate* is crystalline. The *aurochloride* $C_{36}H_{47}NO_{11}HClAuCl_3$ crystallises from alcohol in small needles (Wright a. Luff).

Acetyl-apopseudaconitine $C_{36}H_{46}AcNO_{11}aq$. Formed by heating pseudaconitine at 100° with acetic anhydride or glacial acetic acid, and separated by agitation with ether. Crystalline. Nitrate and aurochloride crystalline. *Benzoyl-apopseudaconitine* $C_{36}H_{46}BzNO_{11}aq$. Indistinctly crystalline. Nitrate and aurochloride crystallise, the latter from alcohol in anhydrous rosettes (W. a. L.).

Pseudaconine. $C_{27}H_{41}NO_9$ [100°]. Formed, together with veratric acid, by heating pseudaconitine with dilute mineral acids, or better with alcoholic soda. Light yellow varnish, moderately soluble in water forming a strongly alkaline bitter solution, which, however, does not produce any prickly sensation on the tongue. Soluble in ether. Forms amorphous salts. Reduces silver solution and alkaline copper solution when heated.—$C_{27}H_{41}NO_9HIHgI_2$ is a white amorphous precipitate (W. a. L.).

Apopseudaconine $C_{27}H_{39}NO_8$. Formed, together with veratric acid, by heating pseudaconitine with alcoholic soda at 140°. Closely resembles pseudaconine.—$C_{27}H_{37}Ac_2NO_8$ is an amorphous varnish melting below 100°, sparingly soluble in water. Salts amorphous. $C_{27}H_{37}Bz_2NO_8$ is nearly insoluble in water (W. a. L.).

4. **Japaconitine.** $C_{66}H_{88}N_2O_{21}$. In the root of *Aconitum Japonicum*. Prepared by exhausting the root with alcohol containing 1 p.c. tartaric acid, concentrating the extract when adding water, and repeatedly agitating the filtered liquid with ether to remove resinous constituents; precipitating the alkaloids with sodium carbonate; agitating it with ether; dissolving it in aqueous tartaric acid; again precipitating it with Na_2CO_3, and dissolving in ether. The resulting solution when left to evaporate deposited crystals which after being freed from adhering syrup, were re-crystallised from ether, and after repeated fractional crystallisation gave by analysis numbers agreeing with the formula $C_{66}H_{88}N_2O_{21}$, confirmed by the analysis of the gold-salt. The *hydrobromide* $C_{66}H_{88}N_2O_{21}\,2HBr\,5H_2O$, and the *nitrate* crystallise well (Wright a. Luff, *C. J.* 35, 387).

Japaconine, $C_{26}H_{41}NO_{10}$, is obtained, together with benzoic acid, by heating japaconitine with alcoholic potash: $C_{66}H_{88}N_2O_{21} + 3H_2O = 2C_7H_6O_2 + 2C_{26}H_{41}NO_{10}$. Yellowish varnish, easily soluble in ether, alcohol, and chloroform; insoluble in water. Forms a mercuriodide $C_{26}H_{41}NO_{10}HIHgI_2$.

Japaconitine and japaconine heated with benzoic anhydride yield the same product, viz. $C_{26}H_{39}NO_7(OC_7H_5O)_4$, which is flocculent, dissolves in ether, and does not crystallise. Salts non-crystalline, nitrate very sparingly soluble in water (W. a. L.).

5. **Lycaconitine** $C_{27}H_{34}N_2O_6\,2aq$. A non-crystallisable alkaloid obtained from wolf's bane, *aconitum lycoctonum* (Dragendorff a. Spohn, *J. Ph.* [5] 10, 361; *C. J.* 48, 403). If heated with water under pressure it is converted into crystalline *lycoctonic acid*, $C_{17}H_{18}N_2O_7$, and two alkaloids, *lycaconine* and *acolyctine*.

6. **Myoctonine**, $C_{27}H_{30}N_2O_8\,5aq$. Is an amorphous alkaloid also present in *A. lycoctonum*.

H. W.

ACONITIC ACID $C_6H_6O_6$ *i.e.* $C_3H_3(CO_2H)_3$ or $CO_2H.CH_2.C(CO_2H):CH.CO_2H$ [186°-187°] S. 18·6 at 13°. S. (80 p.c. alcohol) 50 at 12°. *Equisetic acid, citridic acid.* Occurs as calcium salt in the roots and leaves of monk's-hood (*Aconitum Napellus*) and other aconites, in the herb of *Delphinium Consolida* collected after flowering (Wicke, *A.* 90, 98); in the horse-tail (*Equisetum fluviatile*) (Baup, *A.* 77, 293); in millefoil (Zanon, *A.* 58, 21; Hlasiwetz, *J. pr.* 72, 429); in the juice of the sugar-cane (Behr, *B.* 10, 351), and in that of sugar-beet (O. v. Lippmann, *B.* 12, 1649); as calcium and potassium salt in the leaves of *Adonis vernalis* (Linderos, *A.* 182, 365).

Formation.—1. By the action of heat on citric acid, or by prolonged boiling of that acid with hydrochloric acid: $C_6H_8O_7 - H_2O = C_6H_6O_6$ (Dessaignes, *C. R.* 42, 494); more quickly by heating citric acid with HCl in a sealed tube at 130°-140° (Hergt, *J. pr.* [2] 8, 372), or by boiling it with HBr (Mercadante, *G.* 7, 248).—2. In small quantity, together with citraconic acid, by heating citric acid with HI in a sealed tube (Kämmerer. *A.* 139, 269).

Preparation.—Citric acid, in portions of 100 grams each, is heated in small flasks provided with bent distillation-tubes ⅓ met. long, till the whole tube is lined with small oily drops, and the residue is heated on a water bath with 15 g. water till it solidifies to a crystalline mass. On pulverising this mass and treating it with pure ether, aconitic acid dissolves and citric acid is left behind (Pawolleck, *A.* 178, 150). Hunäus (*B.* 9, 1751) heats citric acid at 140° for a day in a stream of HCl-gas, dissolves the product in a small quantity of water, evaporates, and treats the residue by Pawolleck's method.

Properties and *Reactions.*—Crystallises in small four-sided plates, melting at 187° and resolved at the same time into CO_2 and itaconic acid $C_5H_6O_4$; also when heated with water at

180° (Pebal, *A.* 98, 94). Dissolves easily in absolute ether, whereby it is distinguished from citric acid. Converted by *sodium-amalgam* into tricarballylic acid $C_6H_8O_6$ (Hlasiwetz, *J.* 1864, 396). Unites with fuming HBr, at 100°, forming bromocitric acid $C_6H_7BrO_7$, and with hypochlorous acid, forming chlorocitric acid $C_6H_7ClO_7$. The calcium salt fermented with cheese yields succinic acid (Dessaignes, *C. R.* 31, 432).

Salts. The acid is tribasic. The NH_4, K, Na, Mg and Zn salts dissolve readily in water, the rest are insoluble or only sparingly soluble. The soluble aconitates form, with lead and silver solutions, white flocculent precipitates (distinction from fumaric and maleic acids).

$(NH_4)H_2A'''$: nodules or laminæ. S. 15·4 at 15°.—$(NH_4)_2HA'''$.—$K_3A'''2aq$. S. 9 at 15° (Baup, A. 77, 299). Slender, silky, very deliquescent needles; lose aq at 100° and aq at 190° (Guinochet, *C. R.* 94, 455).—K_2HA''' 2aq. S. 37·7 at 16°: small prisms (G.).—KH_2A'''. S. 11 at 17°; minute elongated prisms.—Na_3A''' 2aq: retains its water in a current of air at 60° but gives it up at 15° *in vacuo*.—Li_3A''' 2aq: v. sol. water; solution is alkaline.—$CaHA'''aq$: gummy; v. sol. water.—$Ca_3A'''_2$ 3aq: gummy; v. sol. cold water, but at 80°-100° this solution deposits rhombic prisms, sl. sol. cold water. The latter gradually dissolve, changing to the gummy variety.—$Ca_3A'''_2$ 6aq. S. 1·01 at 15° (B.).—$Sr_3A'''_2$ 3aq. S. ·625 at 16° (G.). Ppd. on boiling the solution.—$BaH_4A'''_2$: prisms. S. 4·2 at 17° (G.).—$Ba_3A'''_2$ 3aq: gelatinous pp. got by adding $BaCl_2$ to aconitic acid or a solution of an aconitate.—$Mg_3A'''_2$ 3aq. S. 10·4 at 17°. Elongated octahedra (G.).—$Co_3A'''_2$ 3aq. S. 3·5 at 16°. Pink powder.—$Ni_3A'''_2aq$. Pp. changed by long boiling to $Ni_3A'''_2$ 6aq.—$Cd_3A'''_2$ 6aq. S. ·113 at 17°. Prisms.—$Zn_3A'''_2$3aq: insoluble in water.—$Pb_3A'''_2$ 3aq(?): flocculent precipitate (Buchner).—$Pb_3A'''_2 2PbO 2H_2O$: obtained by prolonged boiling of the NH_4-salt with basic lead acetate (Otto, *A.* 127, 180).—$Mn_3A'''_2$ 12aq: small rose-coloured octahedra, slightly soluble in water (Baup).—Ag_3A''' prepared by adding $AgNO_3$ to the normal ammonium salt, is a thick flocculent precipitate, becoming crystalline on drying; slightly soluble in water.

A solution of aconitic acid mixed with ferric chloride is precipitated by ammonia, but the presence of citric acid even in small quantity prevents the precipitation (*Bn.* 1, 648).

Ethers.—The ethers of aconitic acid are formed by heating the acetyl derivatives of the corresponding citric ethers, $C_3H_4(OAc)(CO_2R)_3$, at 250°-280°, acetic acid being split off; yield 75 p.c. of the theoretical (Anschütz a. Klingemann, B. 18, 1953).

Me_3A''' (271°) (Hunæus, *B.* 9, 1750); (161°) at 14 mm. (A. a. K.) From aconitic acid, MeOH, and HCl (H.).

Et_3A''' (275°) (Mercadante, *G.* 1, 248); (252°) at 250 mm. (Conen, *B.* 12, 1655); (171°) at 14 mm. (A. a. K.). S.G. $\frac{20}{4}$ 1·1064 (C.); $\frac{14}{}$ 1·074 (Crasso, *A.* 34, 59). From tetra-ethyl citrate and PCl_5 at 100° (Conen).

Pr_3A''' (195°) at 13 mm. (A. a. K.)

Di-anilide. [217°]. Yellow needles; formed by boiling aqueous aniline aconitate (Michael, *B.* 19, 1374).

Iso-aconitic ether
$CO_2Et.CH:CH.CH(CO_2Et)_2$(?)(248°) S.G. $\frac{18}{18}$ 1·0505. A product of the action of hot HCl upon di-carboxy-glutaconic ether (*q. v.*). An oil; sol. alcohol or ether (Conrad a. Guthzeit, *A.* 222, 255).

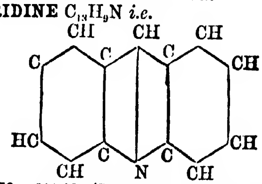
Pseudo-aconitic acid
$CO_2H.CH_2.CH(CO_2H).C''.CO_2H$ [217°]
Formed at 180° from propylene tetra-carboxylic acid (*q. v.*), obtained from bromo-maleic ether and sodium malonic ether (Schacherl, *A.* 229, 95).

Salt.—$Ba_3A'''_2aq$. H. W.

ACORIN $C_{36}H_{60}O_6$. A glucoside extracted from the common reed (*Acorus calamus*). Sol. alcohol or ether; ppd. by benzene from its ethereal solution (A. Faust, *Bl.* [2] 9, 392; Thoms, *Ar. Ph.* [3] 24, 465).

ACRALDEHYDE *v.* ACROLEÏN.

ACRIDINE $C_{13}H_9N$ *i.e.*



M. w. 179. [106°] (Bernthsen); [111°] (Fischer a. Körner). V. D. 6·10 (Graebe, *B.* 5, 15).

Occurrence.—In coal tar (Graebe a. Caro, *A.* 158, 265). The portion that boils between 300° and 360° is extracted with H_2SO_4Aq and the extract ppd. by $K_2Cr_2O_7$.

Formation.—1. By heating formyl-diphenylamine (23 g.) with $ZnCl_2$ (45 g.) at 190°-220°:
$$H.CO.N(C_6H_5)_2 = C_{13}H_9N + H_2O.$$
2. From crystallised oxalic acid, diphenylamine, and $ZnCl_2$ at 120°-260°.—3. From chloroform, diphenylamine, and $ZnCl_2$ or $AlCl_3$. In this way 2 g. of acridine can be got from 25 g. diphenylamine. It is better to heat chloroform (1 pt.) with diphenylamine (1 pt.), $ZnCl_2$ (1 pt.), and ZnO (½ pt.), for 8 hrs. at 200° (Fischer a. Körner, *B.* 17, 101). $(C_6H_5)_2NH + CCl_3H + ZnO = C_{13}H_9N,HCl + ZnCl_2 + H_2O$. — 4. By passing phenyl-*o*-toluidine through a red hot tube (Graebe, *B.* 17, 1370).—5. In small quantity (5 p.c.) by heating aniline and $ZnCl_2$ with *o*- or *p*- oxy-benzoic aldehyde or even with benzoic aldehyde (Möhlau, *B.* 19, 2151).

Preparation.—Heat formic acid (50 g. of S.G. 1·22) with diphenylamine (175 g.) and $ZnCl_2$ (100 g.) gradually from 150° to 270°, avoiding evolution of CO. Dissolve the product in alcohol, and pour into aqueous NaOH. Acridine and diphenylamine are in the alcoholic layer; evaporate this, and dissolve the residue in ether; shake the ether with dilute hydrochloric acid. The acridine is then in the acid solution. The yield is small (Bernthsen, *A.* 224, 3).

Properties.—Long needles (from much water) or prisms, $a:b:c = ·656:1:·335$. Pungent odour and burning taste. The base and its hydrochloride attack the tongue even when in minute quantities. Volatile with steam. Very slightly soluble in water. Dilute solutions exhibit a characteristic greenish-blue fluorescence.

Salts.—(Bernthsen, *A.* 224, 3; *B.* 16, 1802 Graebe, *B.* 16, 2828; Medicus, *B.* 17, 196.)—B'HCl: yellow plates, soluble in water imparting a bluish-green fluorescence.—$B'_2H_2PtCl_6$: sparingly soluble minute yellow needles.—

B'_2HNO_2 3aq: [151°], yellow pp. got by adding sodium nitrite to a solution of an acridine salt. Long yellow silky needles; sl. sol. ether or cold water, m. sol. hot water, v. e. sol. alcohol; somewhat volatile with steam.—$B'_2H_2SO_3$: formed by adding aqueous SO_2 to a solution of the hydrochloride. Yellowish-red needles, v. sl. sol. water.—$B'HNaSO_3$: got by mixing solutions of sodium sulphite and acridine hydrochloride. Colourless, easily soluble, prisms.

Picrate. $C_{13}H_9NC_6H_2(NO_2)_3OH$. Minute yellow prismatic needles. Melts at a high temperature. V. sl. sol. cold alcohol, cold water or cold benzene. Boiling water partially decomposes it (Anschütz, *B.* 17, 438).

Acridine forms no carbonate.

Reactions.—1. $HgCl_2$ gives a yellow crystalline pp. $(C_{13}H_9N,HCl)_2HgCl_2$.—2. $K_2Cr_2O_7$ gives a yellow pp. $C_{13}H_9NH_2CrO_4$.—3. I dissolved in KIAq gives a brownish pp. $(C_{13}H_9NHI)_2I_2$.—4. *Reduced* in alcoholic solution by sodium amalgam to hydro-acridine which is soluble in alcohol; at the same time a white powder insoluble in alcohol is formed. *Hydro-acridine*, $C_6H_4\Big<{CH_2 \atop NH}\Big>C_6H_4$, is not a base. It forms prisms, [169°], sl. sol. cold alcohol, v. sol. hot alcohol or ether, insol. water. Sol. conc. H_2SO_4 and reppd. by water, unaltered. It is oxidised by Ag_2O or CrO_3 back to acridine.—5. $KMnO_4$ *oxidises* acridine to a quinoline di-carboxylic acid (acridinic acid) (Graebe a. Caro, *B.* 13, 99).

Octo-hydro-acridine (*acridine-octo-hydride*) $C_{13}H_{17}N$ [84°]. (320°). Colourless plates or tables. Formed by heating acridine or hydroacridine with HI and P at 220°.—B',HCl: colourless tables, soluble in hot water, sparingly in cold (Graebe, *B.* 16, 2831).

ACRIDINES.—Compounds having the general formula

$$C_6H_4\Big<{CR \atop N}\Big>C_6H_4.$$

They are characterised by basic properties, fluorescence in dilute solutions, capability of directly uniting with MeI, and of forming neutral dihydrides which may readily be reconverted into the original base. *v.* BUTYL-ACRIDINE, METHYL-ACRIDINE, and PHENYL-ACRIDINE. See also AMIDO-PHENYL-ACRIDINE, OXY-PHENYL-ACRIDINE, AMIDO-HYDRO-ACRIDINE KETONE.

ACRIDINIC ACID *v.* (*Py.* 2:3)-QUINOLINE-DI-CARBOXYLIC ACID.

ACRIDYL-BENZOIC ACID *v.* PHENYL-ACRIDINE CARBOXYLIC ACID.

ACROLACTIC ACID

$C_3H_4O_3$, *i.e.* $CHO.CH_2.CO_2H$ or $CH(OH):CH.CO_2H$. Formed by boiling ethyl β-chloro-acrylate $CHCl:CH.CO_2Et$, with baryta water (Pinner, *B.* 7, 250; *A.* 179, 91). The acid is a thick syrup. Its silver salt, AgA', blackens quickly on exposure to light, and is m. sol. water.

ACROLEÏN C_3H_4O, *i.e.* $CH_2:CH.CHO$. *Acrylic aldehyde, Acraldehyde.* Mol. w. 56. (52·4°). V.D. 1·897. S. 2·5. S.G. $\frac{20}{4}$ ·841; μ_β 1·4089; R_∞ 25·31 (Brühl).

Formation.—1. By oxidation of allyl alcohol $CH_2:CH.CH_2OH$, with platinum-black or chromic acid mixture.—2. By dehydration of glycerin, $C_3H_8O_3$, and therefore in the destructive distillation of fats.—3. By distillation of acetone dibromide: $C_3H_6OBr_2 = 2HBr + C_3H_4O$.—4. From di-iodacetone and silver cyanide (M. Simpson, *J. pr.* 102, 380).—5. By exploding ethylene with a large excess of oxygen, the carbon being partly oxidised to CO, which with the ethylene forms acraldehyde, $C_2H_4 + CO = C_3H_4O$. This effect, however, is produced only by nascent, not by ready-formed CO (E. v. Meyer, *J. pr.* [2] 10, 113).

Preparation.—Anhydrous glycerin (1 pt.) is distilled with $KHSO_4$ (2 pts.), and the vapour, after passing over calcium chloride and lead oxide to remove water and acrylic acid, is condensed by a freezing mixture (Aronstein, *A. Suppl.* 3, 180).—Obtained also in large quantity as a by-product in the preparation of œnanthaldehyde, from castor-oil (Schorlemmer).

Properties.—Mobile strongly refracting liquid. Vapour extremely irritating to the nose and eyes. Taste pungent and burning. It is readily converted into disacryl, a white amorphous body (isomeric or polymeric?), insoluble in water, alcohol, acids, and alkalis.

Reactions.—1. Oxidised quickly in the air, or by silver-solution to acrylic acid, in the latter case with formation of a silver speculum; by nitric acid to glycollic and oxalic acids (Claus, *A. Suppl.* 2, 118).—2. Converted by nascent *hydrogen* (Zn and HCl) into allyl alcohol, C_3H_6O, isopropyl alcohol, C_3H_8O, and acropinacone $2C_3H_4O + H_2 = C_6H_{10}O_2$ (Linnemann, *A. Suppl.* 3, 257).—3. With PCl_5 acroleïn yields allylene chloride $C_3H_4Cl_2$ (84·5°), the isomeric dihydrochloroglycide or β-epidichlorhydrin (102°), and trichlorhydrin $C_3H_5Cl_3$ boiling at 152°–156° (Geuther, *Z.* 1865, 24).—According to Romburgh (*Bl.* [2] 36, 549) the three liquids are allylidene chloride $C_3H_4Cl_2$ (85°), its isomeride, (110° cor.), and β-chloro-allyl alcohol $CHCl:CH.CH_2OH$ (153° cor.).—4. *Bromine* forms di-bromo-propionic aldehyde (*q. v.*).—5. Acroleïn heated with *ethyl-alcohol* and its homologues and a little acetic acid, yields glycerides; *e.g.* triethylin $C_3H_5(C_2H_5)_3O_3$, from 1 vol. C_3H_4O and 1 vol. alcohol and 0·5 vol. acetic acid; trimethylin $C_3H_5(CH_3)_3O_3$, from 1 vol. C_3H_4O, 3 vol. methyl alcohol, and 0·5 vol. acetic acid; and triamylin $C_3H_5(C_5H_{11})_3O_3$, in like manner. On passing HCl-gas into a mixture of acroleïn and 2 vol. absolute alcohol, diethylchlorhydrin $C_3H_5(C_2H_5)_2ClO_2$ is obtained as a heavy oil having a sweetish ethereal odour and S. G. 1·03 at 10·5° (Alsberg, *J.* 1864, 494).—6. Acroleïn acts strongly on *aniline*, forming diallylidene-di-phenyl-di-amine, $(C_6H_5)_2(C_3H_4)_2N_2$ (Schiff, *J.* 1864, 414).

Combinations.—1. With Sodium Hydrogen Sulphite by direct combination $C_3H_4O,2NaHSO_3 = CH_3.CH(NaSO_3).CH(OH)(NaSO_3)$. Crystalline nodules. With acids gives off SO_2 but no acroleïn. By NH_3 and $BaCl_2$ only half the sulphurous acid is precipitated as $BaSO_3$, the α-sulphopropionic aldehyde remaining in solution. Sodium amalgam converts it into oxypropane sulphonic acid. Silver oxide oxidises it to α-sulpho-propionic acid (Max Müller, *B.* 6, 1441.—*Bn.* 360).

2. With Acetic Anhydride. $C_3H_4O,C_4H_6O_3$ or $C_3H_4(OAc)_2$. Formed by direct combination at 100°. Liquid (180°). S.G. ^{22} 1·076 (Hübner a. Geuther, *A.* 114, 47).

3. With Acetyl Chloride. $C_3H_4O,2C_2H_3OCl$. Liquid boiling at 140°–145° (Aronstein).

4. With Ethyl Chloride. CH_2:CH.CHCl(OC_2H_5). Formed together with acroleïn-acetal, by the action of sodium ethylate on allylidene chloride, CH_2:CH.$CHCl_2$ at 120°. Liquid. (115°-120°).

5. With Ethyl Alcohol. $C_5H_{10}O_2$ *i.e.* CH_2:CH.CH(OH)(OC_2H_5). From acroleïn hydrochloride and sodium ethylate:

CH_2:CH.CHO,HCl + NaOEt =
NaCl + CH_2:CH.CH(OH)OEt.

Liquid boiling, with partial decomposition at 130°. S.G. º 0·946. Soluble in water, alcohol and ether (Geuther a. Cartmell, *A.* 112, 3).

6. With ammonia, acroleïn forms a condensation-product $C_6H_9NO = 2C_3H_4O + NH_3 - H_2O$, prepared by passing the vapour of anhydrous acroleïn into alcoholic ammonia (Hübner a. Geuther, *A.* 114, 35), or more readily by passing the vapour of crude acroleïn into aqueous ammonia, expelling the excess of ammonia by a gentle heat and precipitating the remaining liquid with a mixture of ether and alcohol (Claus. *A.* 130, 186).—Red amorphous body easily soluble in water and in acids, sparingly in hot alcohol, insoluble in cold alcohol and in ether. Converted by dry distillation, first into a non-volatile oxygenated base (Claus. *A.* 158, 222), then into picoline and water (Baeyer, *A.* 155, 283). Acroleïn-ammonia unites directly with bases, forming brown amorphous salts. The *platinochloride* $(C_6H_9NOHCl)_2PtCl_4$ is a yellow amorphous pp.

Polymerides. 1. Metacroleïn $(C_3H_4O)_3$. [50°]. V.D. 5·9. Formed with evolution of hydrogen, when acroleïn hydrochloride is heated with potassium hydroxide (not NaOH). Needle-shaped crystals lighter than water, having an aromatic odour. Partly reconverted by distillation into acroleïn. Volatilises undecomposed with aqueous vapour. Insoluble in cold, sparingly soluble in hot water, easily in alcohol and ether. Exerts only a feeble reducing action on ammoniacal silver solution. Not affected by dilute alkalis, but changed more or less into acroleïn by heating with mineral acids. Does not combine with ammonia. Unites with dry HCl-gas forming β-chloropropionic aldehyde $CH_2Cl.CH_2.CHO$ (Geuther a. Cartmell, *A.* 112, 3).

2. Acroleïn resin. Formed by heating acroleïn for a week with 2-3 vol. water at 100°, as a brown resin which begins to melt at 100°, is moderately soluble in hot water, easily in alcohol and in ether. Heated with ammoniacal silver solution, it reduces the silver in specular form. Reconverted into acroleïn at 100° (G. a. C.).

3. Hexacroleïc acid $C_{18}H_{24}O_6$. Formed by treating acroleïn with alcoholic or aqueous potash or with moist silver oxide. Yellow amorphous body, insoluble in water, easily soluble in alkalis, alcohol, and ether. Has a slight acid reaction. Salts: $NaC_{18}H_{23}O_6$: brown and amorphous. $Ca(C_{18}H_{23}O_6)_2$: yellow flocculent precipitate, insoluble in water and in alcohol. *Barium salt*; amorphous; decomposed by CO_2 (Claus. *A. Suppl.* 2, 120). II. W.

ACROLEÏN-DIPHENYLAMINE *v.* DI-PHENYL-AMINE-ACROLEÏN.

ACROLEÏN-UREA $C_4H_8N_2O$, *i.e.* $CON_2H_2(C_3H_4)$.

Formed by the action of acroleïn on urea in alcoholic solution (Leeds, *A.C.J.* 4, 58; *B.* 15, 1580). White powder; sol. alcohol, ether, or CS_2. Other bodies are also formed (Schiff, *A.* 151, 206; *B.* 15, 1898).

ACROLEÏN-*m*-XYLIDINE *v.* *m*-XYLIDINE ACROLEÏN.

ACROPINACONE $C_6H_{10}O_2$, *i.e.* CH_2:CH.CH(OH).CH(OH).CH:CH_2 (160°-180°) S.G. ^{17} ·99. Formed by action of zinc and dilute H_2SO_4 upon acroleïn (Linnemann, *A. Suppl.* 3, 268; L. Henry, *J. pr.* [2] 9, 477). It is extracted with ether. It turns brown in air. V. sol. alcohol or ether, insol. water.

ACROTHIALDINE. $C_9H_{13}NS_2$5aq. A base produced by the action of ammonium sulphydrate on acroleïn at 0° (Schiff, *Bl.* [2] 8, 444). Insol. water, v. sl. sol. alcohol, ether, or CS_2.

ACRYL-COLLOIDS *v.* β-BROMO-ACRYLIC ACID.

ACRYL-ALDEHYDO-PHENOXY-ACETIC ACID $C_{11}H_{10}O_4$ *i.e.* CHO.CH:CH.C_6H_4.O.CH_2.CO_2H *o* [153°]. *m* [100°]. *p* [182°]. These three acids are prepared by adding a cold aqueous solution of aldehyde to a dilute solution of sodium *o*-aldehydo-phenoxy-acetate at 50° (Elkan, *B.* 19, 3018).

ACRYLIC ACID $C_3H_4O_2$, *i.e.* CH_2:CH.CO_2H. Mol. w. 72. [8°] (140°) (Linnemann, *A.* 171, 294).

Formation.—1. By oxidation of acroleïn (p. 61).—2. By heating β-iodopropionic acid with sodium ethylate: $CH_2I.CH_2.CO_2H$ + NaOEt =
NaI + EtOH + CH_2:CH.CO_2H.
(v. Schneider a. Erlenmeyer, *B.* 3, 339).—3. By heating β-iodopropionic acid with lead oxide.—4. Together with propyl alcohol and other products, by heating allyl alcohol with KOH (Tollens, *Z.* [2] 6, 457).—5. From iodoform and sodium ethylate (Butlerow, *A.* 114, 204).—6. By debromination of α-β-dibromopropionic acid with zinc-dust,

$CH_2Br.CHBr.CO_2H - Br_2 = CH_2$:CH.$CO_2H$.

7. By heating dichlorallylene with water:

CCl_2:C:CH_2 + $2H_2O$ = 2HCl + CH_2:CH.CO_2H

(Pinner, *B.* 7, 66).—8. By the distillation of hydracrylates $C_3H_6O_3 = C_3H_4O_2 + H_2O$ (Beilstein, *A.* 122, 372).

Preparation.—Acroleïn mixed with 3 vol. water is poured upon recently precipitated silver oxide suspended in water in a vessel protected from light; the liquid is heated to boiling; sodium carbonate added to slight alkaline reaction; and the mass, after evaporation to dryness, is treated with dilute sulphuric acid. The liquid is filtered (hexacroleïc acid and reduced silver remaining on the filter) and the filtrate is distilled, acrylic acid then passing over (Claus. *A. Suppl.* 2, 117).

Properties.—Colourless liquid having a pungent odour like that of acetic acid; solidifying at low temperatures; miscible with water.

Reactions.—1. Converted by *sodium-amalgam* and by boiling with *zinc* and dilute *sulphuric acid* into propionic acid (Linnemann, *A.* 125, 317).—2. Fusion with KOH gives formic and acetic acids: $C_3H_4O_2 + 2H_2O = CH_2O_2 + C_2H_4O_2 + H_2$ (Erlenmeyer, *A.* 191, 376).—3. Unites directly with *bromine* forming αβ-dibromopropionic acid, $CH_2Br.CHBr.CO_2H$, and with *hydriodic acid*, forming β-iodopropionic acid, $CH_2I.CH_2.CO_2H$ (Wislicenus, *A.* 166, 1).—4. Its alcoholic solution saturated with HCl, yields ethyl β-chloropropionate, $CH_2Cl.CH_2.CO_2C_2H_5$ (Linnemann, *A.* 163, 96).—5. Unites with *hypochlorous acid*, forming β-chlorolactic acid

$CH_2 : CH.CO_2H + ClOH = CH_2Cl.CHOH.CO_2H$ (Mellikow, *B.* 12, 2227; 13, 2154).

Salts.—All except the silver salt are easily soluble in water. Give off part of their acid at 100°, leaving basic salts; the K-, Ba-, and Zn-salts decomposing in this manner even at ordinary temperatures.—$KC_3H_3O_2$ is very deliquescent (Clausius).—NaA′, microscopic needles. 100 pts. cold alcohol dissolve 0·7 pt. of this salt (Zotta, *A.* 192, 105). Dissolves easily in 90 p.c. alcohol. Melts with decomposition above 250° (Linnemann). Converted by heating with aqueous soda at 100° into the isomeric hydracrylic acid $CH_2OH.CH_2.CO_2H$ (Linnemann, *B.* 8, 1095).—CaA'_2: needles (Caspary a. Tollens).—SrA'_2: small rhombic plates very soluble in water.—ZnA'_2: small scales (Clausius).—PbA'_2: shining needles soluble in alcohol.—AgA′: flocculent precipitate crystallising from boiling water in prisms (Caspary a. Tollens, *A.* 167, 240).

Ethers.—MeA′ (80·3°) (Weger) S.G. $\frac{0}{0}$ ·934. From methyl α-β-di-bromo-propionate, MeOH, Zn and H_2SO_4 (C. a. T.; Kahlbaum, *B.* 13, 2319).—EtA′ (98·5°) (W.); (101·5°) (C. a. T.). From ethyl α-β-di-bromo-propionate, EtOH, Zn and H_2SO_4.—PrA′ (122·9°) (W.). From propyl α-β-di-bromo-propionate, PrOH, Zn and H_2SO_4.—*Allyl ether.* C_3H_5A' (119°–124°) (C. a. T.).

Other derivatives of acrylic acid are described as: Bromo-acrylic acids, Chloro-acrylic acids, Chloro-bromo-acrylic acid, Amido-acrylic acid, Bromo-iodo-acrylic acid, Iodo-acrylic acid. See also Hydracrylic acid.

Paracrylic Acids $(C_3H_4O_2)_n$.—An acid probably having this composition is formed by the action of potassium cyanide on ethyl α-chloro-propionate at 150°. Short prisms melting at 180°–182°. Gives a brown red pp. with ferric chloride (Karetnikoff, *J. R.* 9, 116).—Another paracrylic acid is formed by boiling aqueous β-iodopropionic acid with excess of silver oxide, till the solution becomes coloured, and metallic silver begins to separate. The same acid is formed when hydracrylic acid $C_3H_6O_3$ is left in contact for several days with 1 mol. bromine.—Small crystals melting at 69°; insol. in water, slightly sol. in cold, easily in hot, alcohol. Easily takes up HI at 157° and is converted into β-iodopropionic acid.—The sodium salt is indistinctly crystalline, deliquescent, does not melt at 180°. The lead salt is soluble in water (Klimenko, *J. R.* 12, 102).

Di-acrylic acid $C_6H_8O_4$.

At 250° sodium hydracrylate is decomposed into water, sodium acrylate, and sodium di-acrylate. On treating this mixture with water it becomes very hot, and the sodium di-acrylate takes up aq being converted into para-adipomalate, $Na_2C_6H_8O_5$. The latter is thrown down as a viscid syrup when an equal volume of alcohol is added. At 200°-250° it loses aq, changing to sodium di-acrylate, an amorphous deliquescent mass, which becomes warm when breathed upon, combining again with aq. **Salts.**—Na_2A''.—BaA″.—CaA″: from calcic hydracrylate at 220° (Wislicenus, *A.* 174, 285).

Para-adipomalic acid is a syrup. It is reduced by HI to para-adipic acid $C_6H_{10}O_4$. **Salts.**—$Na_2C_6H_8O_5$ aq.—BaA″.—CuA″ aq.—PbA″. All are amorphous. H. W.

ACTINOMETER.—Instrument for measuring chemical intensity of light. *V.* Physical Methods, sect. Optical.

ADENINE $C_5H_5N_5 3aq$. Occurs amongst the decomposition-products of the contents of all growing animal and vegetable cells. Formed, amongst other products, by boiling nucleïn with dilute H_2SO_4.

Long rhombic needles (from NH_3Aq. (V. sol. hot water, and in NaOHAq, v. sl. sol. Na_2CO_3Aq. Neutral to litmus. Insol. ether or $CHCl_3$.—By nitrous acid it is converted into hypoxanthine (Kossel, *B.* 18, 79, 1928; *H.* 10, 248). $C_5H_3Ag_2N_5$: insol. NH_3Aq. $(C_5H_5N_5)_2H_2SO_4 2Aq$. Sl. sol. water.

ADIPIC ACID $C_6H_{10}O_4$ *i.e.* $CO_2H.CH_2.CH_2.CH_2.CH_2.CO_2H$. Mol. w. 146. [149°]. S. 1·44 at 15°; S. (ether) ·633 at 19° (Dieterle a. Hell, *B.* 17, 2221); S. 7·73 at 18° (Wirz, *A.* 104, 257).

Formation.—1. By the oxidising action of nitric acid on sebacic acid, and on natural fats, *e.g.* hog's lard, cocoanut oil, &c.—the first product of the action being sebacic acid, which by further oxidation is converted into adipic acid (Laurent, *A. Ch.* [2] 66, 166; Bromeis, *A.* 35, 105; Malaguti, *A. Ch.* [3] 16, 84).—2. By the action of HI and phosphorus at 140° on mucic acid (Crum Brown, *A.* 125, 19), or saccharic acid (De la Motte, *B.* 12, 1572).—3. From muconic acid $C_6H_6O_4$ and sodium-amalgam (Marquardt, *B.* 2, 385).—4. From β-iodopropionic acid and silver at 100°–160°; $2(CH_2I.CH_2.CO_2H) + Ag_2 = 2AgI + (CH_2)_4(CO_2H)_2$ (Wislicenus, *A.* 149, 221). 5. By reduction of di-acetylene di-carboxylic acid, $CO_2H.C{:}C.C{:}C.CO_2H$, or of hydro-muconic acid, $C_4H_6(CO_2H)_2$, with sodium-amalgam (Baeyer, *B.* 18, 680).—6. By heating butane-ω-tetra-carboxylic acid (Perkin, *B.* 19, 2040).

Preparation.—Sebacic acid is boiled with nitric acid, whereby it is converted into a mixture of adipic and succinic acids, which are soluble in water. The nitric acid is then evaporated off, and the residue crystallised from water. It is then fused and the solidified mass is pulverised and treated with ether, which dissolves the adipic acid, leaving a small quantity of succinic acid (Arppe, *Z.* 1865, 300).

Properties.—Monoclinic laminæ, flat needles, or feathery groups of needles. Sparingly soluble in cold water, freely in alcohol and ether. It has a tendency to form supersaturated solutions. Converted into butane by distilling with large excess of CaO (Hanriot, *C. R.* 101, 1156).

Salts.—The *ammonium salt* $(NH_4)_2A''$ forms monoclinic crystals resembling augite; $a:b:c = \cdot688:1:\cdot979$: $\beta = 82°14'$ (*A.* 217, 143). S. 40 at 14°. At 150° it gives off all its NH_3.—$Na_2A''2aq$.—$Na_2A''\frac{1}{2}aq$: very soluble pearly plates.—K_2A''.—BaA″: white pp. S. 12·04 at 12°; 7·47 at 100°. SrA″$\frac{1}{2}$aq.—CaA″aq.—CaA″2aq: minute needles (from alcohol), giving up their water at 100° (Laurent, *C. R.* 31, 351).—MgA″4aq: prisms. S. 25 at 15°.—ZnA″2aq.—CdA″2aq.—CuA″aq.—CuA″2aq.—PbA″: small glistening plates, S. ·021 at 16°.—HgA″: white crystalline pp.—Ag_2A'': small glistening plates, S. ·016 at 14°.—The ferric salt is a brown-red insoluble pp. For more detailed description of salts *v.* Dieterle a. Hell, *B.* 17, 2221.

Ethyl ether.—Et_2A'' (245°) (Arppe, *Z.* 1865, 302).

Amide $C_4H_8(CO_2NH_2)_2$ [220°] S. ·44 (Henry, *Bl.* 48, 618).—*Dimethyl-amide* $C_4H_8(CO_2NHMe)_2$ [151°–153°] (H.).

Derivatives of adipic acid v. BROMO-ADIPIC ACID, OXY-ADIPIC ACID. H. W.

Para-adipic Acid.—Formed by the action of HI on paradipimalic acid, $C_6H_{10}O_5$—a decomposition product of sodium hydracrylate *v. di*-ACRYLIC ACID.—Syrupy.—$ZnC_6H_8O_4,3H_2O$. Viscid flocculent pp. (Wislicenus, *A.* 174, 295). H. W.

Iso-adipic acid $C_4H_8(CO_2H)_2$. [192°]. S. 1 at 22°. A product of the action of bromine on the sulphate of cyanethine (*q. v.*). The product is extracted with ether; on evaporation this leaves an oil which reacts violently with strong NH_3, forming crystals of the amide of butane dicarboxylic acid, $C_4H_8(CONH_2)_2$. Converted by boiling dilute H_2SO_4 or HCl into the acid. (E. v. Meyer, *J. pr.* [2] 26, 358).

Properties.—Rows of prisms, or, from hot concentrated solution in water, globular aggregates. Begins to sublime at 100°. Readily soluble in alcohol and ether.

Salts.—$A''H(NH_4)$. Solutions of this salt give the following precipitates: Fe_2Cl_6, reddish-white; $AgNO_3$, white; $CuSO_4$, green; $Pb(OAc)_2$, on agitation, prisms crossing one another; $HgCl_2$, $CaCl_2$, $BaCl_2$ give no pps.—$A''Ag_2$.—$A''Cu$.—$A''Pb$, $\frac{1}{2}$aq.

Amide.—(See above.)—Does not melt at 260°. Prisms with pyramidal ends (from water).

Adipic acid $C_4H_8(CO_2H)_2$ (*Hydro-pyro-cinchonic acid*) [194°]. Small white needles or glistening prisms; easily soluble in alcohol and ether, less in water. Is the chief product of reduction of pyrocinchonic acid $CO_2H.CMe:CMe.CO_2H$ or of the reduction of di-chloro-adipic acid $CO_2H.CClMe.CClMe.CO_2H$. By conversion into the anhydride and redissolving in water it is converted into the isomeric adipic acid melting at [240°].

Salts.—CaA'' $1\frac{1}{2}$aq: very sparingly soluble white silky needles.—SrA'' $1\frac{1}{2}$aq: sparingly soluble needles.—PbA'' 3aq: white crystalline pp.—$A''Cu$: green pp.

Anhydride.—$\begin{matrix}CH(CH_3).CO\\ \vert \\ CH(CH_3).CO\end{matrix}\!\!>\!O.$ [187°] (Otto a. Beckurts, *B.* 18, 838; Roser, *B.* 15, 2012; Leuckart, *B.* 18, 2344).

Constitution.—Probably identical with the above iso-adipic acid.

Adipic acid $(C_4H_8(CO_2H)_2)_n$ [240°]. Glistening plates, or prismatic needles. Formed by isomeric change from the preceding adipic acid [194°] by conversion into the anhydride and redissolving in water.

Salt.—Ag_2A'': sparingly soluble white crystalline pp. The acid does not give an anhydride on heating (Otto a. Beckurts, *B.* 18, 843).

Adipic acid $C_4H_8(CO_2H)_2$ [165°–167°]. *Di-methyl-succinic acid* (?)—From aceto-acetic ether by means of sodium, α-bromo-propionic ether, and MeI (Hardtmuth, *A.* 192, 142).

Salts.—PbA'': flocculent pp.—Ag_2A''.

Adipic acid $C_6H_{10}O_4$ [142°–143°].—From tropilene (*q. v.*) and HNO_3(S.G. 1·285) (Ladenburg, *A.* 217, 140).

Salts.—Ag_2A''.—Ammonium salt forms triclinic crystals: $a:b:c = \cdot8474:1:\cdot5496$ $\alpha = 90°\ 20'$. $\beta = 95°10'$. $\gamma = 100°\ 50'$.

Constitution.—Probably identical with *u*-di-methyl-succinic acid (*q. v.*), $CO_2H.CMe_2.CH_2.CO_2H$.

Other isomerides of adipic acid are described as METHYL-ETHYL-MALONIC, PROPYL-MALONIC, ISO-PROPYL-MALONIC, DI-METHYL-SUCCINIC, ETHYL-SUCCINIC, and METHYL-GLUTARIC ACIDS.

Adipic (?) aldehyde $C_6H_{10}O_2$.—Formed by treating acetic aldehyde with zinc-turnings at 100° $3C_2H_4O - H_2O = C_6H_{10}O_2$. Smells like wild mint, and appears to be decomposed by prolonged distillation, with formation of H_2O and higher condensation products. Unites with alkaline bisulphites, forming crystalline compounds (Riban, *C. R.* 75, 98). H. W.

ADIPOCERE.—A fatty substance produced in the decomposition of animal substances in moist ground; first found by Fourcroy in the *Cimetière des Innocens* at Paris. Consists of palmitic, stearic, and oleic acids (Gregory, *A.* 61, 362; Wetherill, *J.* 1855, 517). According to Ebert (*B.* 8, 775) it consists essentially of palmitic acid, together with margaric and oxymargaric acids, $C_{17}H_{34}O_2$ and $C_{17}H_{34}O_3$. H. W.

ADIPOMALIC ACID $C_6H_{10}O_5$, is formed by boiling bromadipic acid with potash, as a viscid mass which becomes crystalline.—$PbC_6H_8O_5 5H_2O$. White precipitate which dissolves in hot solution of lead acetate and separates therefrom in nacreous scales. Gives off $2H_2O$ at a moderate heat (Gal a. Gay-Lussac, *C. R.* 70, 1175). H. W.

Para-adipo-malic acid *v. di*-ACRYLIC ACID.

ADIPOTARTARIC ACID $C_6H_{10}O_6$. Formed by heating pulverulent dibromadipic acid with water at 150°. Moderately soluble in alcohol and ether. Much more soluble in hot than in cold water, and separates in monoclinic laminæ. Optically inactive. Solution agitated with KOH yields a crystalline pp. resembling cream of tartar (Gal a. Gay-Lussac). H. W.

ADONIDIN. A glucoside in *Adonis vernalis*, resembling digitalin in physiological action (Cervello, *Ph.* [3] 13, 129; Mordagne, *Ph.* [3] 16, 145).

ADONINIDINE. A poisonous substance in *Adonis cupaniana* (Cervello, *G.* 14, 493).

ÆSCIGENIN $C_{12}H_{20}O_2$. Formed, together with glucose, by passing HCl-gas into a boiling alcoholic solution of telæscin (*infra*)

$$C_{18}H_{30}O_7 + H_2O = C_{12}H_{20}O_2 + C_6H_{12}O_6$$

Indistinctly crystalline powder, insoluble in water, soluble in alcohol. Strong sulphuric acid, in presence of sugar, dissolves it with blood-red colour. Acetyl chloride converts it into a diacetate (Rochleder, *J.* 1867, 751). H. W.

ÆSCINIC ACID $C_{24}H_{40}O_{12}$. Occurs in small quantity in the cotyledons of ripe horse-chestnut seeds. Formed, together with propionic acid, by boiling argyræscin with potash-lye:

$$C_{27}H_{42}O_{12} + 2KOH = KC_{24}H_{39}O_{12} + KC_3H_5O_2,$$

and together with butyric acid by similar treatment of aphrodæscin:

$$C_{52}H_{82}O_{23} + 3KOH = 2KC_{24}H_{39}O_{12} + KC_4H_7O_2.$$

Gelatinous mass, becoming partially crystalline.

Resolved by hydrochloric acid into glucose and telæscin:

$$C_{24}H_{40}O_{12} + H_2O = C_6H_{12}O_6 + C_{18}H_{30}O_7.$$

The acid potassium salt $KC_{24}H_{39}O_{12},C_{24}H_{40}O_{12}$, forms silky needles, sl. sol. water (Rochleder). H. W.

ÆSCIORCEÏN $C_9H_7NO_5$. A substance resembling orceïn, formed by the action of ammonia-vapour on moist paraæsculetin:

$$C_9H_8O_4 + NH_3 + O = H_2O + C_9H_7NO_5$$

(Rochleder, *J.* 1867, 753). H. W.

ÆSCIORCIN $C_9H_8O_4$, is formed by the action of sodium amalgam on æsculetin. Dissolves in alkalis with green colour quickly changing to red. Converted by ammonia into æsciorceïn (Rochleder, ibid. 751). H. W.

ÆSCIOXALIC ACID $C_7H_6O_6,H_2O$. Produced, together with formic and oxalic acids, sometimes also protocatechuic acid, by boiling æsculetin with very strong potash lye. More easily obtained pure by boiling æsculetin for several hours with baryta water in an atmosphere of hydrogen. Very minutely crystalline mass. Gives with ferric chloride a red-brown colour, changing to purple-violet on addition of sodium carbonate; with ferrous sulphate and a small quantity of sodium carbonate, a deep blue colour (Rochleder, *J.* 1867, 752). H. W.

ÆSCULETIC ACID $C_9H_8O_5$, *i.e.* $C_6H_2(OH)_3CH{:}CH.CO_2H$. Formed by boiling æsculetin with baryta (Rochleder, *J. pr.* 69, 211).

Salts.—BaA'_2.—$5PbC_9H_6O_5,C_9H_8O_5$. Acids which contain the group $CH{:}CH.CO_2H$, such as fumaric and maleïc acids and the coumaric acids, are usually capable of existing in two forms, one of which can be easily transformed into the other. Æsculetic acid and its methyl derivatives are at present known in one form only, but tri-ethyl æsculetic acid and its ether have been obtained in two forms, which are described below as derivatives of (α) and (β) æsculetic acid.

Tri-methyl derivative $C_6H_2(OMe)_3.C_2H_2.CO_2H$ [168°]. Needles. Soluble in alcohol, ether, benzene, and hot water, sparingly in cold water. Formed by the action of alcoholic KOH on the following body. Its neutralised solution gives pps. with $AgNO_3$, $CuSO_4$, $ZnSO_4$, and $Pb(OAc)_2$.

Methyl ether $C_6H_2(OMe)_3.C_2H_2.CO_2Me$ [109°]. Prisms. Distils undecomposed at a very high temperature. Soluble in alcohol, ether, and benzene, insoluble in water. Formed by evaporating dimethylæsculetin (1 mol.) with a solution of NaOH (2 mols.) nearly to dryness and digesting the residue dissolved in methyl alcohol with methyl iodide (Tiemann a. Will, *B.* 15, 2082).

(α)-ÆSCULETIC ACID $C_6H_2(OH)_3.CH{:}CH.CO_2H$

Tri-ethyl-derivative $C_6H_2(OEt)_3.C_2H_2.CO_2H$ [103°]. Prepared by saponification of its ether. Changes when heated to its boiling point or boiled with strong HCl into the (β)-isomeride.

On reduction with sodium-amalgam the tri-ethyl-derivatives of both (α)- and (β)- æsculetic acid give the same tri-ethoxy-phenyl-propionic acid, $C_6H_2(OEt)_3CH_2CH_2CO_2Et$, and with alkaline $KMnO_4$ the same tri-ethoxy-benzoic aldehyde, $C_6H_2(OEt)_3CHO$.

Ethyl-Ether $C_6H_2(OEt)_3.C_2H_2.CO_2Et$ [51°], thick yellow prisms, very soluble in alcohol, ether, and benzene, insoluble in water; prepared by heating di-ethyl-æsculetin with sodium ethylate and ethyl-iodide at 100°, avoiding an excess of ethyl-iodide and longer heating than four hours; on heating to its boiling point (above 230°) it changes into the (β)-isomeride (Will, *B.* 16, 2110).

(β)-ÆSCULETIC ACID $C_6H_2(OH)_3.CH{:}CH.CO_2H$

Tri-ethyl-derivative $C_6H_2(OEt)_3.C_2H_2.CO_2H$ [144°], colourless silvery crystals, easily soluble in alcohol, ether, and benzene, nearly insoluble in water; formed by saponification of its ether, or by heating the (α)-isomer to its boiling point.

Ethyl-Ether $C_6H_2(OEt)_3.C_2H_2.CO_2Et$ [75°], glistening tables, easily soluble in alcohol, ether and benzene, insoluble in water, distils undecomposed above 360°; prepared by heating di-ethyl-æsculetin with ethyl iodide and sodium ethylate at 100° for 8 hours; it is also formed by heating the (α)-isomeric ether to its boiling point (Will, *B.* 16, 2108).

ÆSCULETIN

$$C_9H_6O_4,\ i.e.\ C_6H_2(OH)_2\begin{cases} CH{:}CH \\ \quad\ \ \vert \\ O\ .\ CO \end{cases}$$

Occurs in very small quantity in horse-chestnut bark. Formed by the action of dilute acids or of emulsin on æsculin (Rochleder, *J.* 1863, 589).

Preparation.—A solution of æsculin in warm strong hydrochloric acid is boiled till it solidifies to a crystalline pulp; this after washing with water is dissolved in warm alcohol; the solution precipitated with lead acetate; the precipitate of lead-æsculetin is washed with alcohol and afterwards with boiling water, then suspended in boiling water and decomposed by hydrogen sulphide; the liquid is filtered at boiling heat; and the æsculetin which separates on cooling is recrystallised (Zwenger, *A.* 90, 63).

Properties.—Very thin shining needles or scales consisting of $C_9H_6O_4,H_2O$; bitter, slightly soluble in cold, more soluble in warm, water and alcohol, nearly insoluble in ether. Aqueous solution exhibits a very faint blue fluorescence, considerably exalted, however, by addition of a small quantity of ammonium carbonate. Deep green coloration with ferric chloride; yellow precipitate with lead acetate. Æsculetin dissolves in hydrochloric acid; and is oxidised by nitric acid to oxalic acid. By boiling with very strong potash-lye, it is converted into formic, oxalic, protocatechuic, and æscioxalic acids; by sodium amalgam into æsciorcinol.

A hydrate $C_9H_6O_4,\frac{1}{2}H_2O$, isomeric with daphnetin, occurs in horse-chestnut bark in larger quantity than anhydrous æsculetin. It is less soluble in water than the latter, and crystallises therefrom in small granules. Sublimes at 203°, and melts above 250°, converted into æsculetin by heating at 200° in CO_2-stream, also when crystallised from hot hydrochloric acid or from absolute alcohol mixed with strong hydrochloric acid (Rochleder, *J.* 1863, 588).

Æsculetin unites with MgO (Schiff, *B.* 13, 1951), and with solution of lead acetate forms a lemon-yellow precipitate having the composition $PbC_9H_4O_4$ (Zwenger, *A.* 90, 63).

Diacetylæsculetin $C_{13}H_{10}O_6$ *i.e.* $C_9H_4Ac_2O_4$ [134°] formed by treating æsculetin with acetic anhydride and sodium acetate. Crystallises from alcohol in prisms; from water in needles; dissolves in alcohol and ether; is not coloured by ferric chloride; is easily saponified by heating with strong sulphuric acid at 30° to 40° (Nachbauer, *A.* 107, 248).

Bromoæsculetins.—$C_9H_4Br_2O_4$, formed by treating dibromæsculin with strong sulphuric acid, crystallises from alcohol in yellowish needles melting at 233°, slightly soluble in

water.—$C_9H_4Br_2O_4$, formed by adding bromine to a hot solution of æsculetin in glacial acetic acid, crystallises from alcohol in long yellow needles, melting with decomposition at 240° (Liebermann a. Knietsch, *B.* 13, 1591).

Di-acetyl-di-bromo-æsculetin $C_{13}H_8Br_2O_6$ *i.e.* $C_9H_2Ac_2Br_2O_4$ [177°]. Formed by acetylation of di-brom-æsculetin crystallises from alcohol in slender needles.

Di-acetyl-tri-bromo-æsculetin $C_{13}H_7Br_3O_6$ *i.e.* $C_9HAc_2Br_3O_4$, formed by acetylation of tri-bromæsculetin, or by bromination of diacetylæsculetin, crystallises in long very thin needles, melting, with decomposition at 180°–182°; insoluble in water (L. and K.; Liebermann a. Mastbaum, *B.* 14, 475).

Methyl-æsculetin $C_{10}H_8O_4$ *i. e.* $C_9H_4O_2(OH)(OMe)$ [184°] is formed by heating æsculetin (6 pts.) with methyl iodide (15 pts.) and KOH (4 pts.) dissolved in a small quantity of methyl alcohol till the liquid becomes neutral. On treating the product, after the greater part of the methyl alcohol has been given off, with water and hydrochloric acid, methylæsculetin crystallises out, while dimethylæsculetin remains in solution.

Shining needles. Soluble in cold dilute alkalis and in ammonia, and precipitated therefrom by acids. Decomposed by boiling aqueous alkalis like æsculetin. Insoluble in cold, but soluble in hot water; easily soluble in alcohol, ether and benzene, insoluble in light petroleum (Tiemann a. Will, *B.* 15, 2075).

Dimethylæsculetin, $C_{11}H_{10}O_4$ *i. e.* $C_9H_4O_2(OMe)_2$ [144°], is deposited from the mother-liquor of the preceding compound on addition of ammonia. Shining needles. Easily soluble in alcohol, ether, and benzene, nearly insoluble in light petroleum; insoluble in cold, soluble in hot, water. Dissolved by H_2SO_4 and precipitated by water. H. W.

Ethyl-æsculetin $C_9H_4O_2(OH)(OEt)$ [143°], colourless crystals, soluble in alcohol, ether, benzene, alkalis, and hot water, insoluble in cold water.

Di-ethyl-æsculetin $C_9H_4O_2(OEt)_2$ [109°], colourless silvery plates, soluble in alcohol, ether, and benzene, sparingly in hot water, insoluble in cold water and cold aqueous alkalis (Will, *B.* 16, 2106).

Constitution.—Æsculetin contains two hydroxyls, for it forms a di-acetyl derivative. The formation of protocatechuic and of tri-ethoxy-propionic acids and of tri-ethoxy-benzoic aldehyde from æsculetin and tri-ethyl-æsculetic acids respectively show them to be aromatic bodies. If we compare the formulæ for coumarin $C_9H_6O_2$, umbelliferon, $C_9H_6O_3$ and æsculetin, $C_9H_6O_4$, we see that the two latter may be regarded as oxy- and di-oxy-coumarin. That umbelliferon is oxy-coumarin has been proved by synthesis (Tiemann a. Reimer, *B.* 12, 993). All three bodies are fluorescent in alkaline solution, but methyl-umbelliferon, $C_9H_5O_2(OMe)$ and methyl-æsculetin fluoresce more strongly than umbelliferon and æsculetin respectively, while di-methyl-æsculetin, $C_9H_4O_2(OMe)_2$, fluoresces most strongly of all.

When coumarin (1 mol.) is evaporated with NaOH (2 mols.) and the residue digested with MeOH and MeI, it takes up the elements of Me_2O, becoming methylic methyl-*o*-coumarate;

$$C_6H_4\left\langle\begin{array}{l}CH:CH\\ \quad\ \ |\\ O\ .\ CO\end{array}\right. + 2KOH + 2MeI =$$

$$C_6H_4(OK).CH:CH.CO_2K + H_2O + 2MeI =$$
$$C_6H_4(OMe).CH:CH.CO_2Me + H_2O + 2KI.$$

But two isomerides may be got in this way, one, (α), when excess of MeI is avoided and the digestion is for 3 hours at 100°, the other (β) by digesting for a longer time at 150° (W. H. Perkin, *C. J.* 31, 417; 39, 409). Precisely the same reaction occurs when di-ethyl-æsculetin is digested with NaOEt and EtI, the two isomeric ethers, $C_6H_4(OEt)_3.CH:CH.CO_2Et$, being formed, the (α) compound when excess of EtI is avoided and the heating kept up for only four hours, the (β) compound by more prolonged heating. In both cases the (α) compounds are changed by distillation into the (β) compounds. These reactions indicate analogous structure.

It is however, remarkable that di-methyl-æsculetin does not form a dibromide as coumarin does.

Paraæsculetin.—$C_9H_6O_4$ (?).—Obtained by treating æsculetin with aqueous $NaHSO_3$, at boiling heat, then adding rather dilute sulphuric acid and afterwards alcohol, whereby Na_2SO_4 is first thrown down, and then the compound $C_9H_6O_4,NaHSO_3$, which when decomposed by sulphuric acid yields hydrated paraæsculetin $C_9H_6O_4,2\frac{1}{2}H_2O$ in indistinct crystals easily soluble in water, sparingly in ether, more freely in alcohol, less easily in wood-spirit, nearly insoluble in acetone and chloroform, soluble in glacial acetic acid. Paraæsculetin exerts a strong reducing action in alkaline solution, throws down metallic copper from Fehling's solution at 50°-70°, and reduces indigo at ordinary temperature. Not attacked by acetic anhydride. Exposed in the moist state to ammonia-vapour, it quickly turns red, then dingy-violet, and changes after a few minutes to a sky-blue liquid, which when left over sulphuric acid gives off ammonia, and again turns red, from formation of æsciorceïn (p. 65). Converted by heating with aniline into æsculetanilide (Rochleder, *J.* 1863, 589; 1867, 752).

$C_9H_6O_4,NaHSO_3,\frac{1}{2}H_2O$ forms small needles. According to Liebermann a. Knietsch (*J.* 1880, 1028), the true formula of this compound is $C_9H_8O_4,NaHSO_3$; it probably therefore contains a hydro-æsculetin. H. W.

ÆSCULIN $C_{15}H_{16}O_9$ [204·5°–205°] (H. Schiff, *B.* 14, 302).—Occurs in the bark of the horsechestnut (*Æsculus Hippocastanum*) especially in March before the buds open (Minor, *B. J.* 12, 274; Jonas, *A.* 15, 266).

Preparation.—1. Horsechestnut bark is exhausted by boiling with water; the extract is precipitated with lead acetate, and the filtrate, freed from lead by hydrogen sulphide, is evaporated to a syrup. The æsculin then crystallises out after a few days, and may be purified by washing with water, and crystallising, first from weak spirit (40 p.c.), then from boiling water (Rochleder a. Schwarz, *A.* 87, 186).—2. The bark is exhausted with weak aqueous ammonia; the solution evaporated to dryness; the residue, mixed with alumina and exhausted with alcohol of 95 p.c.; and the æsculin which crystallises from the alcohol is agitated with water and

ether, and finally washed with benzene (Fairthorne, *C. N.* 26, 4).

Properties.—Small prisms, composed of $C_{15}H_{16}O_9,2H_2O$? Bitter, sparingly soluble in cold, easily in boiling water, the solution coagulating on cooling. 1 pt. dissolves in 24 pts. boiling alcohol. Very slightly soluble in absolute ether, soluble in glacial acetic acid and ethyl acetate (Trommsdorff, *A.* 14, 200). The aqueous solution is slightly acid, and exhibits a blue fluorescence which disappears on addition of acids, but is restored by alkalis. Dissolves in alkalis more readily than in water.

Reactions.—1. Æsculin is resolved at 230° into glucosan and æsculetin: $C_{15}H_{16}O_9 = C_6H_{10}O_5 + C_9H_6O_4$(Schiff); by digestion with dilute mineral acids or by treatment with emulsin, into glucose and æsculetin (Rochleder a. Schwarz, *A*, 88, 356); by boiling with baryta-water into glucose and æsculetic acid (Rochleder *J. pr.* 69, 211).—2. Converted by sodium-amalgam into hydræsculin (Rochleder).—3. Agitated with a small quantity of nitric acid, it yields a yellow solution which assumes a deep blood-red colour on addition of ammonia, this reaction affords a delicate test for æsculin (Sonnenschein).—3. Conc. H_2SO_4 (4 drops) followed by NaOClAq gives a violet colour (Raby, *J. Ph.* [5] 9, 402).

Æsculin forms with magnesia, the compound $2C_{15}H_{16}O_9Mg(OH)_2$, which is yellow and dissolves readily in water (Schiff, *B.* 13, 1952).

Pentacetylæsculin

$C_{25}H_{26}O_{14}$ *i.e.* $C_{15}H_{11}Ac_5O_9$.

Formed by heating æsculin with acetic oxide crystallises from alcohol in small needles melting at 130° (Schiff, *A.* 161, 73; *B.* 13, 1952).

Di-bromo-æsculin $C_{15}H_{14}Br_2O_9$.

Is obtained by gradually adding bromine in calculated quantity to a solution of æsculin in glacial acetic acid. Crystallises from glacial acetic acid in small needles; melts and decomposes at 193°-105°. Sparingly soluble in alcohol, still less in all other solvents (Liebermann a. Knietsch, *B.* 13, 1591).

Pentacetyl-dibromo-æsculin

$C_{25}H_{24}Br_2O_{14}$ *i.e.* $C_{15}H_9Br_2Ac_5O_9$, prepared in like manner from dibromæsculin, forms slender needles, melting at 203°-206°, converted by strong sulphuric acid into dibromæsculetin.

Pentabenzoylæsculin $C_{50}H_{36}O_{14}$ *i.e.* $C_{15}H_{11}Bz_5O_9$, forms nodular groups of crystals sparingly soluble in ether, freely in hot alcohol (Schiff).

Trianilæsculin

$C_{33}H_{31}N_3O_6$ *i.e.* $C_{15}H_{16}(NC_6H_5)_3O_6$, from æsculin and aniline by prolonged heating at 200°. Amorphous brown powder, soluble with red colour in alcohol (Schiff, *B.* 4, 472). H. W.

ÆTHAL *v.* Cetyl Alcohol.

ÆTHOKIRRIN. The yellow colouring matter of the flowers of *Antirrhinum Linaria.* H. W.

AFFINITY.—Chemical affinity is that property of bodies in virtue of which, when brought into contact, they react on each other, forming new bodies. It can be called a force, in so far as by its action energy is produced, namely, heat, light, electrical or mechanical energy. And, *vice versâ*, energy must be employed to reverse the action of chemical affinity, and to decompose the combined substances.

Nothing is known as yet about the nature of chemical affinity, nor has a satisfactory hypothesis been suggested concerning it. The oldest conceptions concerning the reasons why substances react on each other reach back to Greek philosophy; nothing has survived of them except the name affinity, which preserves the notion that those substances which are of the same origin or of the same kind, and which therefore are as it were related to each other, possess the power of mutual reaction. It is now known that the contrary of this is more correct. Moreover, the reason of the greater or smaller facility with which substances react chemically was conceived to be somewhat similar to human qualities—sympathy and antipathy. These conceptions held sway as long as the philosophy of Aristotle reigned. The breach with these ideas, which was brought about by Galileo's mechanics, introduced mechanical ideas into chemistry also. The ultimate particles of substances were imagined as furnished with points, edges, and hooks, by the aid of which were brought about their decompositions and combinations. Sir Isaac Newton's discovery of the general mutual action of masses introduced a new phase into the conception of nature. The idea of an attractive action between one small particle and another at a distance was introduced by Newton himself into chemistry, in order to explain the mutual reactions of bodies. He did not, however, consider the cause of chemical actions as identical with that of general gravitation, but as different from it, especially as regards the law concerning action at a distance.

Later investigators, Buffon, Bergmann, Berthollet, assumed, on the contrary, that both forces are of the same nature, and that only the circumstances under which chemical forces act—especially the close proximity of the reacting particles—cause an apparent difference.

An influence similar to that due to Newton's astronomical discovery was exerted at the beginning of this century by a physical discovery, that of the electric current. The great chemical activity of the current was soon noticed. By its help Davy decomposed the alkalis and earths; and Berzelius made use of the phenomena of electrical decomposition for the foundation of a theory concerning chemical compounds, which rested on the supposition that chemical attraction was nothing but the attraction of the opposite electricities concentrated on the smallest parts of substances.

The electro-chemical theory of Berzelius was the first chemical theory which was based on facts. Owing to this it obtained great importance. Taking into account the needs of the time, Berzelius developed his theory only with a view towards classification; but it did not contribute anything towards the investigation of the nature of chemical affinity.

The last great change in the views concerning affinity took place in the middle of this century, and was brought about by Mayer's and Joule's discovery of the equivalence of 'forces,' or more strictly, of 'the actions of forces.' It was recognised that chemical affinity was to be classed with mechanical, electrical, and thermal energy, in so far as it is convertible into any of these, and can be produced from each of them

When this was known, the need to trace back the mode of action of the forces of affinity to other known actions of forces ceased to exist, as a great many inferences could be drawn from this experimental fact, and a special hypothesis did not seem called for.

Two different views have been held concerning the way in which chemical forces act, and each of these has still its followers at the present day. First it was imagined that the force acting between two different kinds of matter is similar to that acting between two masses; it brings the ultimate particles nearer together, and, if under the given circumstances this is possible, it produces combination. It would be difficult to entertain different ideas concerning the simple process of combination. The task becomes far more difficult when it is a question of simultaneous decomposition and combination. Very often a substance acts on another which is a compound without combining with it as a whole, but only combining with one of its constituent parts, and expelling the other from the original compound. The hypothesis indicated above refers these facts to the opposite action of two forces, similar to two mechanical forces opposite in direction and unequal in magnitude, which produce motion in the direction of the greater. It was imagined that the stronger chemical affinity overcame the weaker, and produced chemical action in its own direction.

It was in accordance with this conception that 'tables of affinity' were compiled which were to give an account of the force of chemical affinity according to its order. Such tables were first published in 1718 by H. Geoffroy. They contained, under the head of any one substance, a series of others, all of which could enter into chemical combination with the specified body. They were so arranged that the preceding body would always replace all the following bodies from their combinations with the one at the head of the list. Such tables of affinity, which were very popular during the last century, culminated in the works of Bergmann, who collected the ideas indicated above in a theory of affinity. Bergmann recognised that substances can react differently according to circumstances, and therefore he gave two tables for each substance, one for the action in aqueous solution—'in the wet way'; the other for the action at the temperature of fusion—'in the dry way.' Beyond this he kept to the idea that chemical affinity always acts exclusively in one direction, so that under all circumstances a smaller affinity is overcome by a greater.

To Claude Louis Berthollet is due the great merit of having shown this view to be too narrow. According to him, besides 'the intensity of the forces,' the 'mass' of the reacting substances is of importance, in so far as under the same conditions the action is the greater the more of the reacting substances there is present. '*Toute substance qui tend à entrer en combinaison, agit en raison de son affinité et de sa quantité*' (*Statique chimique*, p. 2). This is the concise expression of the new idea which Berthollet introduced into the theory of affinity. But it was reserved for a much later time to develop this idea scientifically, since one of the chief applications which its author made of it—namely, the inference that compounds according to fixed proportions do not exist, but only such as vary in composition within fixed limits—was proved to be false. The proof of this error which was given by Proust, Berthollet's compatriot, brought also the correct foundation into discredit. To this must be added, that in the discoveries of Richter, Dalton, and Berzelius, the science found such important and productive tasks that there was no inducement to investigate what of truth was left in the partially refuted hypothesis of Berthollet. The idea of 'influence of mass' is the first, but not the only, conception which the science owes to Berthollet. This chemist further recognised the decided influence of the physical states of the reacting bodies on the final results of the actions of affinity. He taught that the simple action, according to the measure of affinity and mass, holds only for homogeneous mixtures, but holds no longer when by the appearance of certain substances in a different state of aggregation the chemical equilibrium is disturbed. The influence of '*cohésion*' and '*élasticité*,' on the results of chemical actions, were explained by him perfectly clearly; how first equilibrium is established in the usual manner, but is afterwards disturbed by one of the substances separating out in a different state of aggregation; in consequence of this, a fresh quantity of this substance is formed, and is again separated, and thus the process repeats itself until the substance in question—gaseous or solid—has been entirely, or almost entirely, removed from the changing system. A chemical reaction carried to completion, which had been taken by Bergmann to be the normal case, appears, according to Berthollet, as the exceptional case, and occurs only because of differences in the states of aggregation of the reacting substances.

The decision between these two fundamentally different views has not yet been completely made. Even now, Bergmann's theory is propounded by some investigators, though in a somewhat modified form. In place of the greater or smaller affinity, the greater or smaller production of heat is considered by these investigators as decisive of the course of a chemical action; the fundamental idea, however, the 'exclusiveness' of the reaction, is presupposed by them also. In order to explain those partial reactions in the opposite direction, which certainly occur, those who maintain the theory of Bergmann are obliged to admit that such partial reactions are possible under certain conditions, notably under the influence of heat. These authorities are therefore under the necessity of proving the presence of such special conditions in all those cases wherein we deal with incomplete reactions. Berthollet's theory, on the other hand, by making use of one and the same principle, embraces both kinds of chemical action, and teaches us to consider the one as the limiting case of the other. Apart from this logical advantage it has another; it allows us to apply definite laws, which can be stated in a mathematical form, to the action of affinity taken in conjunction with the action of mass. But this cannot be done by Bergmann's theory, whether in its old or in its new form.

Berthollet's views met with respect and ap-

preciation from his contemporaries, but not with continuation and development; because chemistry began at this time to follow another path which had been opened up by Dalton and Berzelius. Thus it was possible for the fundamental fact of the influence of mass, the fact, namely, that chemical action decreases and increases with the relative quantities of the acting substances, to be denied; and it became necessary to prove this fact at length by many special cases before it could be regarded as a secure property of science. One of the first investigators to whom the merit of this proof is due was H. Rose (*P.* 82, 545), who showed that in the formation of many carbonates of the heavy metals, by precipitating aqueous solutions of the salts of these metals by sodium carbonate, the precipitates contained less carbonic acid and more metallic hydroxide the more water was present in the original solutions. It followed therefore that the water, according to its quantity, expelled the carbonic acid from its combination with the metal. Rose found further (*P.* 94, 481; 95, 96) that when barium sulphate was fused with an equivalent quantity of potassium carbonate it was only partially converted into carbonate. If the quantity of potassium carbonate was increased, appreciably more barium sulphate was decomposed, but only with a proportion of 6 to 7 equivalents did the decomposition become approximately complete.

Another case of the influence of mass was investigated by Bunsen (*A.* 85, 131). If to a mixture of carbonic oxide and hydrogen a quantity of oxygen is added, less than sufficient for the complete combustion of the two gases, a division of the oxygen between the two combustible gases take place. The proportion in which the oxygen combines with either gas depends on the relative masses of these gases. Bunsen's further result, that these proportions can be expressed by some small multiples of the atomic weights of the gases, has been recognised to be an error. Debus (*A.* 85, 103) proved in Bunsen's laboratory the fact of the influence of mass on the precipitation of mixed solutions of lime and baryta by insufficient quantities of carbonic acid. In 1865 Gladstone (*Tr.* 1855, 179; and *C. J.* 9, 54) proved the general truth of the influence of mass in various ways. His method consisted in using certain definite physical properties, especially colour, and the rotation of the plane of polarisation of a ray of light, from measurements of which to draw conclusions concerning the arrangement of compounds in a homogeneous solution. Thus, by comparing the colour of pure ferric sulphocyanide with the colour produced in mixed solutions of iron salts and potassium sulphocyanide, the same amount of iron being present in both solutions, he established the fact, that by the reaction of three equivalents of potassium sulphocyanide and one equivalent of an iron salt, only 13 per cent. of ferric sulphocyanide was formed, and that even in the presence of 375 equivalents of potassium sulphocyanide the whole of the iron had not been converted into sulphocyanide.

By this and similar methods Gladstone established the following laws:

1. When two or more binary compounds are mixed so that all resulting compounds have the power of reacting on each other, each electropositive element enters into combination with each electronegative element, and it does so according to fixed and constant proportions.

2. These proportions are independent of the manner in which the different elements are initially arranged. They are also not only the resultants of the various forces of attraction between the different substances, but depend also on the mass of each of these substances.

3. An alteration in the mass of one of the binary compounds produces a change in the quantity of each of the other binary compounds, and it does so in a ratio which progresses regularly. Sudden changes occur only when a substance can combine with another in more than one proportion.

4. The equilibrium of affinities is generally established after a very short time, but in some cases the elements attain their final condition only after hours.

5. The resulting effects are completely altered when precipitation, volatilisation, crystallisation, and similar phenomena, occur; in such cases the equilibrium which had been established at first is again disturbed by the removal of some of the chemically active substances.

Harcourt and Esson (*C. J.* [2] 5, 460) examined the reaction between hydrogen peroxide and hydriodic acid, and also that between potassium permanganate and oxalic and sulphuric acids. They concluded that 'when any substance is undergoing a chemical change, of which no condition varies except the diminution of the changing substance, the amount of change occurring at any moment is directly proportional to the quantity of the substance.'

The principle, first established by Steinheil (*A.* 48, 153), of determining the chemical composition of a homogeneous liquid by means of physical measurements, was put to practical use by Gladstone in various ways. His measurements might have served as a direct basis of a theory concerning the influence of mass, had such a theory existed. But even the extensive investigations of Berthollet and St. Giles on the etherification of acids and alcohols (*A. Ch.* 61, 65; 66, 68), by which the chemical influence of mass had been confirmed and the magnitude of this influence had been measured, did not give rise to the formulation of a mathematical theory of affinity.

Meanwhile a number of theoretical conceptions, some of old standing, were pointing in the same direction. As far back as 1851 Williamson (*A.* 77, 37; and *C. J.* 4, 110) in his fundamental researches on etherification, had propounded a theory concerning the course of chemical reactions, which explained, better than had been done before, the nature of the chemical influence of mass. According to him, substances which react on each other, when in contact or mixed together, are by no means in a state of neutral equilibrium, but rather in one involving a continuous exchange of constituents. The final result of the reaction depends on the direction in which this exchange of constituents can take place most easily and most frequently. The state of chemical equilibrium arrived at under any conditions is thus not a statical one, in which the forces balance each other and so no more

produce any effect, but is rather a dynamical state, in which two opposite reactions occur continually to the same extent, so that the average state of the system remains the same.

Williamson's theory was accepted for the special case for which it had been propounded. Neither the author nor any of his contemporaries, however, made an application of it to the general explanation of chemical reactions. Meanwhile, hypotheses were developed on an entirely different basis, which agreed with this theory in a most remarkable manner. These are the views concerning the gaseous state, which, first propounded by D. Bernoulli, and afterwards, independently, by Herapath, Joule, Krönig, and Clausius, were developed by Clausius and Maxwell in a mathematically well-founded theory of the states of aggregation. According to this theory, bodies are made up of molecules, which are in a state of continual motion. In the case of gases this motion is rectilinear, until the molecules meet with some resistance, whereby they are caused to rebound according to the laws of collision of elastic bodies. The velocity of motion increases with the temperature, and is inversely proportional to the square root of the molecular weight of the gaseous body. Likewise, there is motion within the molecules, which motion is of the nature of oscillations, the intensity of which bears a constant ratio to the motion of the molecule as a whole. Moreover, at any specified temperature, the molecules of a homogeneous gas have not all the same velocity, but have different velocities varying from the mean value in such a manner that deviations from this value are the fewer the greater they are. In the case of liquids, the molecules have no longer the power of translational motion, but are compelled to fill a definite space owing to the forces which act between them. In other respects the statements made for gases hold good for liquids also, especially those referring to the differences of condition of the various molecules of a homogeneous substance at a constant temperature. The theory has been least developed for the case of solids; here it is to be assumed that the intermolecular forces assign to the various molecules very definite relative positions of equilibrium (v. AGGREGATION, STATES OF, p. 87).

The application of these ideas to chemical processes has been made by L. Pfaundler (*P.* 131, 55). It can easily be seen how they directly lead to conceptions which do not appreciably differ from those of Williamson. The molecular conceptions are, however, a decided improvement on those of Williamson, since, in the differences of the conditions of various molecules, they supply a reason for the continuous interchange of atoms which Williamson supposed to occur. When the velocity of motion exceeds a certain amount, there will always be present some molecules in which this velocity is so great that the connection between the atoms is loosened or destroyed. These molecules are then ready to interchange their constituent atoms, while other molecules, which have a smaller velocity, will not do so. This is the explanation for partial reactions. The same conceptions, when slightly modified, lend themselves to the explanation of the influence of mass and to that of reversible reactions.

At the same time as these hypotheses concerning the mechanism of chemical processes were developed, Guldberg and Waage (*Etudes sur les Affinités chimiques*, Christiania, 1867) laid the foundation for the exact development of the theory of affinity by establishing a mathematical law for the influence of mass. Their work marks an epoch in the history of affinity. It was they who first gave a possibility of determining numerically the intensity of chemical affinities, though at first only as relative magnitudes.

The law established by these two investigators states 'that chemical action is proportional to the active masses of each of the substances participating in the reaction.' By 'active mass' is understood that quantity of the substance participating in the reaction, measured in equivalents or in molecular weights, which is contained in unit volume of the system. This is the same idea as underlay the views of Berthollet; it is the same, only freed from the errors which were attached to it in his time and thrown into an exact mathematical form. Guldberg and Waage lay special stress on the fact that, when the action of several substances on each other is proportional to the active mass of each separately, the intensity of the reciprocal actions among the substances is measured by the product of these masses.

In their earlier paper Guldberg and Waage developed the equations for the chemical equilibrium of opposite reactions by putting the chemical *forces* as proportional to the product of the active masses. On the other hand, as proportional to these same forces they put the *velocities* of the reactions, *i.e.* the relation between the quantity of substance changed and the time necessary to effect the change. In their later papers it was found better to refer the considerations, not to the forces, but to the velocities of the reactions, since these are capable of exact definition, and to leave out of account altogether the somewhat vague idea of chemical forces. According to this conception, chemical equilibrium results when the velocities of the opposite reactions have become equal, *i.e.* when the quantity of substance undergoing a certain change is equal to the quantity formed by the reverse process. It is evident that this is the same theory as had been framed by Williamson, and developed by Pfaundler. The empirical law of the influence of mass thus receives a reasonable foundation in the molecular theory of matter. The effect is proportional to the active mass, because the number of molecules which can react is proportional to the mass. On these lines Van't Hoff (*B.* 10, 669) has deduced the law of the influence of mass. He retains exactly the form given to it by Guldberg and Waage; and in a later paper (*J. pr.* [2] 19, 69) these authors accepted this formal improvement.

In the following part I propose to give a short systematic review of chemical kinetics, or the doctrine of the course of chemical actions, and to deduce from it the conditions and equations of chemical equilibrium; further on, the theoretical conceptions thus gained will be used in the practical determination of the magnitudes of affinities. The theoretical part is based mainly

on the paper of Guldberg and Waage mentioned above. A book recently published by Van't Hoff (*Etudes de Dynamique chimique*) is also of importance, and has been of great use to the author, though he by no means agrees with the whole of its contents.

CHEMICAL KINETICS.—Let us suppose some substance to be undergoing chemical change. Then in any time, dt, some quantity, dx, will have been changed. We define the velocity of the chemical reaction, c, as the ratio of the quantity changed to the time taken for the change, and we therefore put $c=\frac{dx}{dt}$. The quantities of the reacting substances are in every case measured by formula-weights.

The quantity of substance changed will be dependent on many conditions. Among these we find such as are constant, or can be kept constant, during the whole process. Such are temperature, pressure, volume, &c. One condition, namely, the quantity of substance undergoing change, necessarily varies during the process, and we have to find an expression for the velocity of the change as a function of this quantity. This may be done by putting

$$c=\frac{dx}{dt}=kf\ (x_2x_1),$$

where the constant factor k represents the constant conditions, and $f\ (x_1x_2)$ the conditions varying with the quantities $x_1, x_2, \ldots$ Concerning the form of the function $f\ (x_1x_2)$ information has been sought and found in various ways. All the results arrived at are concordant, and show the function to be one of direct proportion. This result has been arrived at empirically, and also theoretically as a deduction from various assumptions. Guldberg and Waage did the first; Horstmann, and others after him, showed that for certain cases, especially for gaseous compounds, the law of direct proportionality between chemical action and mass follows as a necessary consequence from the second law of thermodynamics. Gibbs has made this result perfectly general. The kinetical theory of the constitution of matter leads to the same result, by considering the probabilities for the occurrence of those arrangements of particles which make chemical change possible.

Before, however, the proof for the law of direct proportion between chemical action and mass can be attempted we must distinguish between the various types of chemical reactions. As a rule, chemical action does not take place in the presence of one substance only, but more than one is needed to bring about the final result. Since the final result is proportional to the mass of each separately, we have quite generally

$$\frac{dx}{dt}=k,\ x_1,\ x_2,\ x_3,\ x_4,\ \ldots\ x_n$$

where $x_1, x_2; x_3, \ldots x_n$ are the quantities of the various substances, and x the quantity of substance formed by their reaction. All these quantities are measured according to the ratios of the molecular weights of the various substances.

The simplest case is that in which one substance only undergoes change during the reaction, or that in which the change of only one substance has to be taken into account. The first case occurs when, for example, a substance is decomposed, or when it undergoes a molecular transformation; the second occurs when the other substances participating in the reaction are present in such quantities that the diminution of them occasioned by the chemical change is not appreciable. Since, then, the factors $x_2, x_3, \ldots x$ disappear or become constant, we have

$$c=\frac{dx}{dt}=kx_1.$$

The velocity of the reaction at any instant is proportional to that quantity of substance undergoing change which is still within the sphere of action.

This equation was first established by Wilhelmi (*P.* 81, 413) in 1850 for the inversion of cane-sugar. Since that time it has been confirmed in many ways. In order to compare it with the empirical results it must be integrated. If we put the quantity of substance present at the beginning of the change $=a$, then, after any time t, a quantity x will be decomposed, and, since we are dealing with molecular units, x will at the same time represent the quantity of the product of decomposition formed. The quantity x_1 of substance present at the time t is $(a-x)$, and we have therefore

$$\frac{dx}{dt}=k\ (a-x) \qquad (1)$$

$$\frac{dx}{a-x}=k.dt$$

$$-\log(a-x)=k.t+\text{constant},$$

where *log* represents the natural logarithm. In order to determine the constant of integration, a definite pair of values for x and t must be taken. We put both simultaneously equal to zero, *i.e.* we begin the time from the instant when the decomposition begins, and thence we get

$$-\log a=\text{constant, and}$$

$$\log a-\log(a-x)=\log\frac{a}{a-x}=kt.$$

In order to pass from the natural to the common logarithms we have only to multiply the constant k by its modulus.

Some series of experiments illustrative of this equation will now be given. The first of these refers to a simple decomposition, the change of dibromosuccinic acid into dibromomaleic acid and hydrobromic acid,

$$C_2H_2Br_2(COOH)_2=C_2HBr(COOH)_2+HBr,$$

a change which occurs in aqueous solution at 100°. This reaction has been studied by Van't Hoff (*Etudes de Dynamique chimique*, p. 13). The progress of the decomposition can be traced by titrating with standard alkali. The amount of alkali required for neutralisation before the action began was 10·25 (arbitrary units), and when the change was finished the amount of alkali was 15·32. The excess of alkali used, over 10·21, at any stage of the change is put as equal to x. For a we have 5·11, since two equivalents of dibromosuccinic acid give one equivalent of hydrobromic acid. Van't Hoff's results are presented in the table given on next page. The constancy of the value of k, as shown in the last column, furnishes a proof of the truth of the equation used.

A second series of experiments dealing with the inversion of cane-sugar by means of sulphuric acid is taken from the experiments of W. Ostwald (*J. pr.* 29, 394). The action is one of

t (minutes)	units alkali	x	$\log\frac{a}{a-x}$	k
0	10·21	0·00	—	—
2	10·53	0·32	0·0281	0·0141
4	10·79	0·58	0·0524	0·0131
6	11·05	0·84	0·0776	0·0129
8	11·25	1·04	0·0988	0·0124
10	11·55	1·34	0·1320	0·0132
13	11·94	1·73	0·1795	0·0138
16	12·29	2·08	0·2269	0·0142
19	12·53	2·31	0·2612	0·0138
22	12·84	2·63	0·3116	0·0143
26	13·03	2·82	0·3187	0·0134
30	13·30	3·09	0·4027	0·0135
34	13·57	3·36	0·4647	0·0137
39	13·71	3·50	0·5009	0·0129
45	14·05	3·84	0·6038	0·0135
52	14·32	4·11	0·7077	0·0137
60	14·52	4·31	0·8011	0·0135
71	14·69	4·48	0·9066	0·0128
90	15·03	4·82	1·2141	0·0138

the type called catalytic, *i.e.* the substance which brings about the change (in this case sulphuric acid) does not itself undergo any change. The sugar, by taking up water, is changed into dextrose and lævulose. The rotatory power changes in the same proportion as the decomposition proceeds; the course of the change can therefore be traced by means of the polariscope. The original solution rotated 25°04′; when completely inverted it rotated −8°15′, so that the total angle passed through was 33°19′; this number is at the same time the measure of the total amount of sugar, and must therefore be put $=a$. For x we have the difference $25°01' - w$, where w is the angle of rotation produced by the solution undergoing change at time t.

t (minutes)	w	x	$\log\frac{a}{a-x}$	k
58	20°20	4·81	0·0684	0·0001180
114	16°28	8·76	0·1331	1163
197	11°34	13·70	0·2315	1175
263	8°30	16·74	0·3052	1161
394	3°35	21·69	0·4602	1169
685	−1°33	26·43	0·6909	1182

Similar experiments have been made for many other cases and have given like results. For non-reversible chemical reactions, which depend on the quantity of a single substance only, the above formula holds good quite generally; it can however be proved only in the case of reactions which are sufficiently slow to allow of measurement.

A second main division of chemical processes is formed by those which involve the presence of two different substances. In such cases the general equation (1) takes the form

$$\frac{dx}{dt} = k.x_1.x_2 \qquad (2)$$

Two cases have to be distinguished here; either the quantities of the reacting substances are equivalent with respect to the chemical change considered, or one of them is present in excess. Putting these quantities $= a$ and b, then either $a = b$ or $a > b$. In the first case we have to put $x_1 = x_2 = a - x$ and we get

$$\frac{dx}{dt} = k(a-x)^2 \qquad (3)$$

and integrating

$$\frac{x}{a-x} = a.k.t \qquad (4)$$

where the constant of integration is determined on the same suppositions as before.

Decompositions of this type have often been investigated experimentally. The example given here is a series of experiments by Ostwald (*J. pr.* 27, 1), on the decomposition of acetamide by acids, especially by trichloracetic acid. This change takes place according to the equation:

$$CH_3.CONH_2 + CCl_3.CO_2H + H_2O =$$
$$CCl_3.COONH_4 + CH_3.CO_2H.$$

The quantities both of acetamide and trichloracetic acid diminish, with production of inert ammonium trichloracetate, and acetic acid, which acid under the conditions of the experiment exerts little or no influence on the change. In the following table t stands for the time in minutes, x for the quantity of ammonium salt formed (or, what is the same thing, for the quantity of acetamide decomposed) measured in units such that the total quantity $a = 26·80$.

t	x	$\frac{x}{a-x}$	ak
15	3·13	0·132	0·0088
30	5·52	0·260	0·0087
45	7·61	0·397	0·0086
60	9·23	0·525	0·0088
90	12·01	0·811	0·0090
120	13·82	1·065	0·0089
150	15·51	1·375	0·0092
180	16·59	1·623	0·0090
240	18·33	2·169	0·0090

These results show that the quantity

$$ak = \frac{1}{t} \cdot \frac{x}{a-x}$$

is constant, as is required by theory.

A second series of experiments by R. Warder (*B.* 14, 1361) on the saponification of ethylic acetate gave similar results. Equivalent quantities of ethylic acetate and soda were mixed, and portions taken from time to time were neutralised by dilute acid. The quantities of acid used—these will be called s—give the quantities of the substances not yet decomposed. In each experiment the soda alone would have used 16·00 c.c. of acid; hence we have $a = 16·00$ and $x = 16 - s$, therefore also $a - x = s$

t (minutes)	s	x	$\frac{x}{a-x}$	ak
5	10·24	5·76	0·563	0·113
15	6·13	9·87	1·601	0·107
25	4·32	11·68	2·765	0·108
35	3·41	12·59	3·69	0·106
55	2·31	13·69	5·94	0·108
120	1·10	14·9	13·55	0·113

Again ak is sufficiently constant. When a and b are different, x_1 becomes $a - x$, and x_2 becomes $b - x$; then

$$\frac{dx}{dt} = k(a-x)(b-x) = k\{x^2 - (a+b)x + ab\} \qquad (5)$$

the integral of this equation is

$$\log\frac{(b-x)a}{(a-x)b} = (a-b)kt. \qquad (6)$$

The validity of this equation has been proved by T. Flood (*P. M.* [5] 6, 371).

These two types of non-reversible chemical actions which have been just considered comprise all non-reversible actions which have been accurately studied. To be consistent, we must assume that in chemical reactions which involve more than two, say three, substances, an equation corresponding with those given ought to hold good. Thus when three substances are present in equivalent quantities, $\frac{dx}{dt}=k(a-x)^3$; and

$$\frac{1}{2}\cdot\frac{2ax-x^2}{(a-x)^2}=a^2.kt. \qquad (7)$$

But no reaction has been observed with sufficient certainty the course of which proceeds according to this, or according to a higher, equation.

Moreover, a complication may arise from the simultaneous occurrence of several reactions. For such a case the principle of the 'coexistence of reactions' is important; this principle states that every reaction proceeds as if it alone took place. This principle is of paramount importance; it forms the connecting link between the simple reactions, and those of so-called chemical equilibrium. For the mathematical expression of the coexistence of reactions, when one and the same substance is affected by the various changes, we have the following,

$$\frac{dx}{dt}=k.x_1x_2\ldots+k'x'_1x'_2\ldots+k''x_1''x_2''\ldots$$

If, however, the coexistent reactions take place among different groups, which are themselves without effect on each other, the equation of velocity has to be developed for each separately without regard to the others.

No experimental investigation of the law of coexistence has as yet been published. The application of this law in the theory of affinity leads, however, to results which agree with experience, and the law may therefore be considered to be experimentally proved.

Reversible Reactions.

The processes investigated above frequently represent only one part of the actual reactions. In many cases the substances formed mutually react to reproduce the original substances. In such cases the process does not end with decomposition; but a permanent final state is arrived at in which the original substances, as well as the products of their double decomposition, are coexistent. In such a case the final system is said to be in *chemical equilibrium.* Here we have to consider on the one hand the velocity of the reaction, on the other hand the proportion of the masses for which chemical equilibrium results. As aids in the first part of this inquiry we have the equations given above, together with the principle of coexistence: in investigating the second part of the problem we have the following condition;—*chemical equilibrium results when the velocities of the opposite reactions have become equal.*

The establishment of chemical equilibrium is connected with the second type of chemical reactions [equations (3) (4), and (5) (6)], respectively. For the velocity of each of the reactions we have

$$\frac{dx'}{dt}=k'x_1'x_2', \text{ and } \frac{dx''}{dt}=k''x_1''x_2'';$$

and equilibrium results when

$$\frac{dx'}{dt}=\frac{dx''}{dt} \text{ or } k'x_1'x_2'=k''x_1''x_2''.$$

This is the equation first established by Guldberg and Waage. Putting the initial quantities of the substances as p, q, p', and q', when the substances p' and q' are formed by the reaction of p and q and *vice versâ*, equilibrium will result when a certain quantity ξ of p and q has been decomposed. Then the quantities $p-\xi$, $q-\xi$, $p'+\xi$, $q'+\xi$ are in equilibrium; and ξ has the same value throughout, since the quantities p, q, &c. are measured according to equivalents. The quantity ξ may be positive or negative.

The equation of equilibrium then takes the following form:—

$$k'(p-\xi)(q-\xi)=k''(p'+\xi)(q'+\xi); \qquad (8)$$

from which a value for ξ is found,

$$\xi=\frac{k'(p+q)+k''(p'+q')}{2(k'-k'')}\mp\sqrt{\left(\frac{k'(p+q)+k''(p'+q')}{2(k'-k'')}\right)^2+\frac{k''p'q'-k'pq}{k'-k''}} \qquad (9)$$

The minus sign holds when $\frac{k'}{k''}>1$, and *vice versâ*.

By making certain assumptions, this expression may be considerably simplified. If at the beginning of the reaction the substances p and q only are present, in equivalent quantities, $p=q$ and $p'=q'=o$, and it follows that

$$\frac{k'}{k''}=\frac{\xi^2}{(p-\xi)^2} \text{ and}$$

$$\xi=p\frac{\sqrt{\frac{k'}{k''}}}{\sqrt{\frac{k'}{k''}}+1} \qquad (9a)$$

The equation of velocity takes the following form. The resultant velocity $\frac{dx}{dt}$ is the difference of the partial velocities:

$$\frac{dx}{dt}=k'(p-x)(q-x)-k''(p'+x)(q'+x) \qquad (10)$$

Introducing a new constant h we have

$$h=\frac{k'(p+q)+k''(p'+q')}{k'-k''}-\xi;$$

the equation can then be brought to the form

$$\frac{dx}{dt}=(k'-k'')(\xi-x)(h-x);$$

and from this by integration, we obtain

$$\log\frac{h-x}{\xi-x}\cdot\frac{\xi}{p}=t(k'-k'')(h-\xi) \qquad (11)$$

The form of this equation is analogous to that already deduced for simple reactions (equation (6), p. 72). If now it is assumed, as before, that $p=q$, and $p'=q'=o$, ξ assumes the simple form given in (9a)

$$\text{and } h=p\frac{\sqrt{\frac{k'}{k''}}}{\sqrt{\frac{k'}{k''}}-1}$$

The preceding equations are deductions from the laws of the influence of mass, and the coexistence of chemical reactions. Both laws are of about the same importance in the theory of affinity as the laws of gravitation and the coexistence of motions are in astronomy.

Each individual practical case really comprises several different relations; but there are combinations in which so great a part of the result depends on one single cause, only, that the observed phenomena may be represented almost as if this were the only cause. And as little as we doubt the law of gravitation because the motions of the moon cannot yet be expressed completely in equations, so little have we cause to doubt the laws stated above because certain phenomena cannot yet be represented as simple deductions from them.

We have hitherto assumed that the constant of velocity does not alter its value throughout the whole reaction. It is, however, not impossible that reactions exist in which the reason for the change of k is to be found in the chemical process itself; in such cases the problem becomes considerably complicated.

Chemical Dynamics.

In general dynamics the magnitude of any force is defined and measured by the velocity which it imparts to a mass of known magnitude. Another way of measuring forces consists in establishing equilibrium between the given force and a force acting in the opposite direction, which latter is of a magnitude already known or easily determined. This can be considered as a special case of the first method, as a case in which the velocity due to the given force is reduced to nothing, by means of one equal in magnitude but opposite in direction. The second method, though not a direct one, possesses all the important experimental advantages belonging to a zero method and is therefore the more usual. The measurement of the intensity of chemical forces can be accomplished by two methods, analogous to those employed in general dynamics. The more usually employed method (because of experimental advantages) is the statical, or the method of equilibrium, in which a chemical process is reduced in a certain proportion by another action occurring in the opposite direction. This corresponds to the statical method used in measuring mechanical forces. Analogous to the kinetical method, or the method of velocity, is the process of obtaining a measure of the intensity of the acting forces by measuring the velocity of the chemical change. The two chemical methods are connected in a similar manner as the two mechanical methods, since, as has been shown above, the equilibrium of chemical changes can be regarded as the consequence of the mutual counteraction of changes which are equal in magnitude, but opposite in direction.

Statical Methods.

The first attempts to measure affinities were made by Wenzel, in 1777 (*Die Lehre von der Chemischen Verwandtschaft*, p. 28, Dresden, 1777). He used the method of velocities, but his process was very imperfect. His experiments related to the solution of metals by various acids. Later experiments dealt almost exclusively with the affinity between acids and bases, and were mostly carried out by the method of equilibrium.

Solutions of acids and bases were mixed in proportions such that different acids competed for an insufficient amount of a base, or *vice versâ*; and an attempt was then made to determine the distribution of the base between the competing acids (or *vice versâ*). Ordinary analyses could give no information as to this distribution; since such analyses could determine only the absolute quantities of the acids and bases, and not their distribution. Steinheil (*A.* 48, 153) (although with an entirely different aim) was the first to show how we must proceed in order to get a knowledge of the arrangement of the constituents of a solution without interfering with its composition. Since each of the constituents of a solution changes the physical properties—such as density, refractive index, colour, &c.—of the solution, a knowledge of the laws governing these changes indicates how to solve the problem, by measuring a sufficient number of constants and forming the necessary equations.

It has been already explained how Gladstone used these means for establishing a number of facts concerning the chemical statics of solutions of salts. He could not, however, utilise his measurements further, as there did not then exist a general theory of chemical affinity. Such a theory was first given by Guldberg and Waage (*Etudes sur les Affinités chimiques*, Christiania, 1867) and was also applied by them to a number of measurements. This theory has met with such wide confirmation that we hope to be able some day to reconcile with it those facts which do not appear at present to be in keeping with it.

J. Thomsen (*P.* 138, 65) was the first to apply the theory of Guldberg and Waage to the case of homogeneous solutions. He found that sulphuric acid when acting on soda gives a heat-production of 31,378 gram-units, while nitric acid gives 27,234 units only. Now, when sulphuric acid and nitric acid simultaneously act on soda, all three substances being present in equivalent quantities, three cases may arise. Either the sulphuric acid exclusively combines with the soda, or the nitric acid exclusively does so, or the soda divides itself between the two acids in some fixed proportion. In the first case 31,378 gram-units of heat, and in the second case 27,234 units, would be produced, while in the third case the heat-production would be represented by a number between these two. Therefore the number found by experiment gives a measure of the distribution of the soda between the acids.

Similarly sodium sulphate is allowed to react with nitric acid. If no chemical action results there will be no production of heat. If the nitric acid combines with all the soda, liberating all the sulphuric acid, a disappearance of heat must result, numerically equal to the difference between the two heats of neutralisation; that is to say, $31,378 - 27,234 = 4,144$ units of heat will disappear. If, however, a division of the base between the acids results, a quantity of heat less than 4,144 units will disappear. Experiment shows that 3504 units of heat are used; therefore the soda divides itself between the two acids.

If no secondary thermal action takes place between the substances used in the experiment, we can deduce directly from these numbers that $\frac{3504}{4144} = 0{\cdot}845$ of the total quantity of sodium sulphate is decomposed. Free sulphuric acid does,

however, react with sodium sulphate, and the action is accompanied by production of heat. The extent of the reaction depends on the relative quantities of the reacting substances present. Thomsen has measured this effect for a great many proportions, and has expressed his results by the equation:

$$Q = -\frac{n}{n+0\cdot8}.3{,}300 \text{ gram-units of heat;}$$

where n represents the number of equivalents of sulphuric acid present for each equivalent of sodium sulphate. By the help of this formula Thomsen found empirically that soda divides itself in such a proportion that $\frac{1}{3}$ of it goes to the sulphuric acid, and $\frac{2}{3}$ of it to the nitric acid. Calculating the heat production on this supposition, the result is $-3{,}547$; experiment gives $-3{,}504$; the difference lies within the limit of experimental error.

Guldberg and Waage's theory gives an extremely simple expression for this case. Since sodium sulphate and nitric acid were present in equivalent quantities at the beginning of the reaction, but sodium nitrate and sulphuric acid were absent, we have to put in equation (8)

$$p=q=1 \text{ and } p'=q'=0;$$
$$\text{this gives } k(1-\xi)^2=k'\xi^2,$$
$$\frac{k}{k'}=\frac{\xi^2}{(1-\xi)^2}$$

As ξ is the quantity of soda combined with the nitric acid, and $(1-\xi)$ that combined with the sulphuric acid, it follows that the ratio of the velocities of the reaction is equal to the square of the ratio of distribution. Thomsen calls the endeavour of the acids to combine with bases the *avidity* of the acids, and defines it by the ratio of distribution. According to this, the avidity of sulphuric acid is half as great as that of nitric acid, or putting the latter $=1$, the avidity of sulphuric acid is $=0\cdot5$. The *avidities* are in the ratio of the square roots of the velocities of reaction.

Thomsen (*Thermochemische Untersuchungen*, i. 308) has made further experiments concerning the avidity of other acids towards soda, using a method similar to that described above. His numbers are given in the following table, where the avidity of nitric acid has been put $=1\cdot00$.

Hydrochloric acid .	=1·00
Hydrobromic " .	0·89
Hydriodic " .	0·79
Sulphuric " .	0·49
Selenic " .	0·45
Trichloracetic " .	0·36
Orthophosphoric acid .	0·25
Oxalic " .	0·24
Monochloracetic " .	0·09
Hydrofluoric " .	0·05
Tartaric " .	0·05
Citric " .	0·05
Acetic " .	0·03

Boric, silicic, and hydrocyanic acids do not give any appreciable values.

Taking the squares of these numbers we get the relative velocities of the reactions between the acids and the soda, which values cannot be obtained directly owing to their great magnitude.

The question now presents itself as to whether the *avidities* thus found have constant values, or whether they change when a base other than soda is employed. Thomsen made similar experiments for hydrochloric and sulphuric acids, using different bases (*P.* 138, 497); viz. potash, ammonia, and magnesia, the oxides of manganese, iron, cobalt, nickel, zinc, and copper; for the avidity of sulphuric acid he obtained numbers which increase from 0·5 up to 0·8, and vary, for the alkalis between 0·5 and 0·57, and for the bases of the magnesia series between 0·70 and 0·81. These results induced Thomsen to conclude that the relative avidity of acids depends on the nature of the base.

Berthelot (*A. Ch.* [4] 30, 516), however, raised the just objection that Thomsen's method does not allow of the measurement of the relative avidities without the introduction of errors. The free sulphuric acid reacts on the neutral salt, forming acid sulphate, and thus loses part of its active power, and it does this the more the greater the quantity of acid-sulphate which can be formed.

Thomsen's experiments were repeated by W. Ostwald (*P. Ergzbd.* 8, 167; *J. pr.* [2] 19, 468), who used a different method based on measuring the changes of volume which accompany chemical reactions in aqueous solutions. The volume of the solution of a salt is different from the sum of the volumes of the solutions of the acid and the base, which by their mutual action produce the salt; and further this change of volume is different for different bases and acids. If we use solutions which contain one gram-equivalent of the acid or base per kilogram of solution then the volume of two equivalents of soda is 1913·26 c.c., and that of two equivalents of nitric acid is 1933·25 c.c.; the sum of these two is 3846·51 c.c.; but the volume of the corresponding solution of sodium nitrate is 3886·05 c.c., that is to say, 39·54 c.c. more than the sum of the volumes of acid and base. Repetition of the experiment with sulphuric acid gives an increase of volume of 29·96 c.c. only. Hence the volume-changes can be used for determining the composition of the solution, in the same manner as the heats of neutralisation had been used by Thomsen. Results were obtained by this method exhibiting the behaviour of nitric acid and sulphuric acid towards soda; these results agreed entirely with those of Thomsen. Thomsen's conclusion that nitric and hydrochloric acids are stronger acids than sulphuric acid—a result opposed to the older views—was thus confirmed by Ostwald. The same chemist investigated at length the question as to whether the relative affinity of an acid varied with the nature of the base. By experiments to which Berthelot's objection cannot apply, he arrived at the result that *the relative avidity of an acid is independent of the base.* Thus with hydrochloric and nitric acids he found the following numbers:—

Potash . .	0·97
Soda . . .	0·96
Ammonia . .	0·96
Magnesia . .	0·99
Zinc oxide .	0·95
Copper oxide .	0·97

The differences are not greater than the probable errors of the experiment.

The question concerning the influence of temperature on the relative affinities of acids has also been investigated by Ostwald. He

measured the expansion due to heating the same solutions which had served for the volumetric experiments with soda. The ratio of the avidity or affinity of hydrochloric acid to that of nitric acid towards soda proved to be as follows:—

At 0°	.	1·02
20°	.	0·96
40°	.	0·98
60°	.	1·00

In both cases the number for sulphuric acid is not quite constant; but, as already mentioned, this acid seems to be the stronger the less acid sulphate is formed, and *vice versâ*.

At a subsequent time Thomsen (*Thermoch. Unters.* i. 89) also attacked the problem of the influence of temperature on relative avidities, and arrived at the same results as Ostwald.

The refraction of light was used by Ostwald as another method for determining the composition of a homogeneous solution by means of its physical properties. Dale and Gladstone (*T.* 1863, 317), and also Landolt (*P.* 133, 1), showed that the function $v(n-1)$, in which n is the refractive index and v the specific volume of a liquid body, depends only on the elementary composition of the body and not on the temperature, nor (within certain limits) on the chemical arrangement of the constituents of the body. Hence the specific volume is inversely proportional to the refractive index diminished by 1, and the volume-changes attendant on chemical reactions must be accompanied by opposite changes in the refractive indices. Experiment has most fully borne out these conclusions. The optical method is, however, less accurate than the volumetric method, when the ordinary apparatus only is used.

The numerical results of Ostwald's experiments are collected in the following table. The numbers have the same meaning as those of Thomsen given before (p. 75), *i.e.* they give the relative avidities of the various acids, putting that of nitric acid = 1.

Acid		Thomsen
Nitric	1·00	1·00
Hydrochloric	0·98	1·00
Trichloracetic	0·80	0·36
Dichloracetic	0·33	—
Monochloracetic	0·070	0·09
Glycolic	0·050	—
Formic	0·039	—
Citric	0·033	—
Acetic	0·0123	0·03
Propionic	0·0104	—
Butyric	0·0098	—
Isobutyric	0·0092	—
Succinic	0·0145	—
Malic	0·0282	—
Tartaric	0·052	0·05

Thomsen's values have also been given as far as they refer to the acids considered here. They agree as well as can be expected; trichloracetic acid alone shows an appreciable difference. Thomsen's number for this acid is undoubtedly much too small; this has been proved beyond doubt by other measurements.

The ratios of avidities given in the preceding table remain the same whether determined for potash, soda, or ammonia; they are independent of the nature of the base.

Besides these three methods which are of general application to the case of solutions, some investigators have employed others, which can, however, be used only in special cases. Thus G. Wiedemann (*W.* 5, 45) has shown that from the magnetic properties of ferric salts in solution we can argue as to the amounts of these salts decomposed by the water into free acid and colloidal soluble iron oxide. This method is, however, restricted to the case of these special salts. A. Müller (*P. Ergzbd.* 6, 123) has drawn conclusions from the change in colour as to the distribution of iron oxide between hydrochloric acid and sulphuric acid. Jelett (*I.* 25, 371) determined the relative affinities of codeine, quinine, and brucine, by means of the rotation of the plane of polarisation, and found for the influence of mass the same law as had been established by Guldberg and Waage. The experiments of Dibbits (*P. Ergzbd.* 7, 462), Brücke (*Sitz. W.* 77, April 1877), and others, are of a more qualitative nature.

Besides these statical methods, based on the determination of the composition of a homogeneous solution, others are available in which the chemical reactions take place in heterogeneous media, viz. between solids and liquids, or liquids and gases, or lastly between solids and gases. The theory of these methods has been also given by Guldberg and Waage, and Ostwald has developed the methods for the purpose of determining affinities.

According to Guldberg and Waage the chemical action of solids in contact with solutions is independent of their mass; in other words, the *chemical mass* of the solids is constant. Otherwise the laws of the influence of mass hold good. If, for example, an acid acts on the salt of another acid, which latter salt is insoluble in water (or more strictly, scarcely soluble), and with the base of which the first acid forms a soluble salt, then the same equation holds good as applies in the case of substances which are all soluble, with this exception that the term corresponding to the insoluble salt becomes constant or independent of x. Putting in the equation $k.p.q = k'.p'.q'$ p = hydrochloric acid, and q = calcium oxalate, then p' = calcium chloride, and q' = oxalic acid.

If the experiment is arranged so that hydrochloric acid acts on an excess of calcium oxalate and that undissolved calcium oxalate is always present, then at all stages of the change oxalic acid and calcium chloride are present in equivalent quantities. Putting the original quantity of hydrochloric acid = 1, and that of the oxalate dissolved = ξ, the equation becomes

$$k(1-\xi)c = k'.\xi.\xi;\text{ hence}$$

$$\frac{k}{k'} = \frac{\xi^2}{c(1-\xi)},\text{ and }\sqrt{\frac{k}{k'}} = \phi = \frac{\xi}{\sqrt{c(1-\xi)}}$$

where c stands for the constant chemical mass of calcium oxalate. In this equation k, k', and c are unknown, while ξ can be measured directly. Repeating the experiment with a different acid, say nitric acid, a new expression of the form

$$\phi_1 = \frac{\xi_1}{\sqrt{c(1-\xi_1)}}$$

is obtained, in which c has the same value as referring to calcium oxalate, which is used in both experiments under the same conditions. Dividing the one equation by the other we get the relative affinities

$$\phi:\phi_1 = \frac{\xi}{\sqrt{1-\xi}} : \frac{\xi_1}{\sqrt{1-\xi_1}}$$

expressed in quantities which can all be directly measured. This method has been used by W. Ostwald and his pupils for determining the relative affinities of various acids, and has given results which agree well with those found for homogeneous solutions. It has great experimental advantages over the physical methods, as the ordinary methods of chemical analysis can be used. The insoluble, or scarcely soluble, salts used were these; *zinc sulphide, calcium oxalate, zinc oxalate, barium chromate, cream of tartar*, and the *sulphates of barium, strontium*, and *calcium*. As a rule the coefficients of affinity thus determined for various salts agree very well amongst themselves, but there are some deviations which are not yet fully explained.

As an example of the method the following numbers are given (*J. pr.* [2] 28, 493); these numbers were obtained by the action of acids on calcium oxalate, a substance lending itself particularly well to these experiments. Experiments were made both with normal and decinormal solutions of acids. Nitric acid is again put = 1.

Acid	Normal	$\frac{1}{10}$ Normal
Hydrochloric	1·00	0·98
Hydrobromic	0·95	0·99
Nitric	1·00	1·00
Chloric	1·04	1·00
Sulphuric	0·70	0·74
Formic	0·0259	0·129
Acetic	0·0105	0·735
Monochloracetic	0·051	0·213
Dichloracetic	0·183	0·188
Trichloracetic	0·612	0·899
Lactic	0·041	0·133
Succinic	0·0205	0·093
Malic	0·0505	0·121
Tartaric	0·0462	0·141
Citric	0·0306	0·144

The numbers in the first column, which refer to normal solutions (one gram-equivalent in a litre), agree well with those before obtained by the volumetric method. Along with them is given a second series referring to solutions ten times as dilute. While the stronger acids exhibit scarcely any change by the dilution, the values for the weaker acids have increased very considerably, and this the more the weaker are the acids. We shall consider this phenomenon at length later on, and find the general law underlying it.

Of further results which have been arrived at by this method one must be noticed as important, viz. that the action of the acids varies as they are present alone or along with their neutral salts (*J. pr.* [2] 28, 209).

Some such result was to be expected in the case of dibasic acids which combine with their neutral salts to form acid salts. The monobasic acids, however, exhibit no tendency to combine with their neutral salts, and yet they too show a change which in the case of the strong acids, such as hydrochloric and nitric, is an increase in the affinity. This increase is proportional to the quantity of the neutral salt present, and decreases rapidly with increasing dilution. This statement does not, however, hold for all monobasic acids, but only for the strong acids. The weak monobasic acids, on the contrary, are considerably more weakened by the presence of their neutral salts, and this the more the weaker are the acids. These facts are of great importance in the interpretation of experiments undertaken for the purpose of determining the relative affinities of acids by the division of a base between two competing acids. Since in this case the acids always act in presence of their own salts, this condition doubtlessly exerts some influence, making the strong acids appear stronger and the weak acids appear weaker. This shows that too much importance must not be attached to the numerical values obtained by the preceding methods; they certainly give the order of the affinities correctly, but the numerical values deviate from the true value in the sense that the large numbers are too large and the small values are too small. We shall see later on that other determinations of the same quantities, which are more likely to give the true values, show deviations in this sense from the above numbers.

Kinetical Methods.

The second way of measuring the intensity of chemical forces is based on determinations of the velocities of the reactions produced by these forces. The theoretical introduction concerning this method has been already considered, and we have seen that many reactions proceed according to a course which agrees well with that calculated from the influence of mass.

This method does not, however, lend itself to direct applications to the majority of the reactions investigated by the statical method. This statement applies particularly to the effects of affinity between acids and bases, because these processes are of too short duration to allow of measurements being accurately made of their velocities. If, however, the magnitudes in question can be measured by kinetical methods, this is because of a general and important principle.

It has been already shown that the nature of the base exerts no influence on the relative avidities or affinities of the acids which react with the base. If the affinity between an acid a and a base b is designated by $f(a, b)$, then the following equations hold good:

$$\frac{f(a, b)}{f(a', b)} = \frac{f(a, b')}{f(a', b')} = \frac{f(a, b'')}{f(a', b'')}.$$

These equations can be true only if each expression $f(a, b)$ is the product of two factors one of which depends on the acid only and the other on the base only; $f(a, b) = \phi(a).\psi(b)$.

The affinity between acids and bases is therefore the product of *specific affinity-coefficients*. All reactions due to acids and bases as such must, on this view, be proportional among themselves. From this it follows that processes which, taken by themselves, have

nothing to do with the formation of salts, may be employed for finding numerical values for the affinities which come into play during the formation of salts, provided the reactions in question have been accomplished by the acids and bases only. Determinations of the specific affinity-coefficients of acids and bases are thus of the greatest importance. It will be our task to show first that the above conclusions are verified by experiment, and then to use the numbers thus arrived at for drawing further deductions.

The first reaction which was used to check the values of the coefficients of affinity of acids determined in the statical way, by means of a kinetical method, was the change of acetamide into ammonium acetate (Ostwald, *J. pr.* [2] 27, 1), which takes place according to the equation $CH_3CONH_2 + H_2O = CH_3COONH_4$. When water only is present the reaction does not proceed to a sensible extent, but when an acid is added the latter exerts a *predisposing* influence, and the process takes place to the degree which is possible under the existing conditions of affinities, concentration, and temperature.

By 'predisposing affinity' is usually understood the cause of reactions between certain substances, which reactions could take place, but do not actually occur, without the presence of another substance, which has affinity towards one of the possible products of the reaction. In the case just discussed, water and acetamide do not react unless an acid capable of combining with the ammonia produced (or a base which has affinity for acetic acid) is present. The strange assumption expressed in the name *predisposing affinity*, viz. that the affinity of the predisposing substance towards a body not yet formed induces the other substances to produce this special body, has been given up, since the molecular theory of Williamson and Clausius, as developed by Pfaundler, gives a much more simple view of such reactions. When applied to the case just considered, this theory tells us that the atoms which form the molecules of acetamide and water only very seldom get a chance of forming ammonium acetate during the movements and collisions of the molecules in question, since the forces which tend to retain the original condition of the system are greater than the forces which tend towards decomposition. If, however, a strong acid or base is added, the forces tending towards decomposition are correspondingly increased, and, in many collisions, in which previously no change occurred, decomposition now takes place (*v.* also Mendeléeff, *B.* 19, 456).

The experiments were conducted by keeping equivalent quantities of acetamide and acid for some time at 65° and 100°. The quantity of ammonium salt formed was determined by decomposing it with sodium hypobromite and measuring the volume of nitrogen evolved. The reaction takes place in the presence of acids, such as hydrochloric acid, according to the equation,

$$CH_3CONH_2 + H_2O + HCl = CH_3COOH + NH_4Cl.$$

Three different kinds of molecules are therefore always necessary for the reaction. Moreover, only two substances, acetamide and hydrochloric acid, undergo an appreciable change of mass during the reaction. The water is present in such excess (about 800 H_2O to 1 HCl) that the change in its mass is unappreciable. Hence, if there are no secondary reactions, the change will proceed according to equations (3) and (4). An example in which the actual reaction agrees with theory has already been given.

But the reaction is by no means free from secondary changes. Particularly (as has been already noticed), the presence of the neutral ammonium salt of the acid added has the effect of increasing the strength of strong acids, and decreasing the strength of weak acids. Consequently when strong acids are used the process is accelerated, compared with its normal value, and the acceleration is the greater the further the change has proceeded. With weak acids, on the other hand, the process is retarded. Owing to the formation of acid salts, the polybasic acids are influenced by similar but much more pronounced secondary reactions. All these conditions have to be taken into account in the investigation of the progress of the reaction, as is seen most conspicuously in the graphical representation given in the original paper. These circumstances are disadvantageous if it is desired to make absolute determinations of the velocity of the reaction, but they are of advantage in the comparison of the kinetical and statical methods, since the results obtained by the latter are also influenced in the same way by similar sources of error.

The time taken to convert half the acetamide into the ammonium salt was taken as the reciprocal measure of the velocity of the reaction. The velocity in minutes was found to be as follows:—

Acid	At 65°	At 100°	Ratio
Hydrochloric	72·1	4·98	14·5
Nitric	75·2	5·35	14·4
Hydrobromic	74·0	5·14	14·4
Trichloracetic	112·8	—	—
Dichloracetic	433·7	—	—
Monochloracetic	4,570	—	—
Formic	28,950	2,138	13·6
Sulphuric	180	14·1	12·8
Oxalic	1,516	118·6	12·8
Tartaric	35,310	929	14·7
Malic	—	—	—
Succinic	—	7,976	—
Citric	44,810	3,088	14·5
Phosphoric	—	3,880	—
Arsenic	—	4,005	—

In order to make these numbers comparable with the coefficients of affinity as found by the volumetric method they must be referred to HCl = 1, by dividing the times corresponding to the several acids each into that corresponding to hydrochloric acid. The relative velocities of the reaction are thus obtained for hydrochloric acid = 1. Further it must be borne in mind that by theory the ratio of the affinities is equal to that of the square roots of the velocities of the reaction. In the following table I have collected the acids the relative affinities of which are known. Under I. are given the velocities of the reaction, under II. their square roots, and under III. the relative affinities:—

Acid	I.	II.	III.
Hydrochloric .	1·00	1·00	0·98
Nitric . .	0·96	0·98	1·00
Hydrobromic .	0·97	0·98	0·95
Trichloracetic .	0·639	0·80	0·80
Dichloracetic .	0·166	0·41	0·33
Monochloracetic	0·0169	0·13	0·07
Formic . .	0·00266	0·052	0·039
Acetic . .	0·000547	0·0234	0·0123
Sulphuric . .	0·428	0·65	0·67
Tartaric . .	0·00564	0·075	0·052
Malic . .	0·00218	0·0467	0·0282
Succinic . .	0·00065	0·0255	0·0145

The numbers in the two last columns agree as well as could be expected. The deviations are in the direction of a greater value for II. than for III. in the case of weak acids. The reason for this lies in the fact that in the enunciation of the equation of velocity no attention was paid to the acetic acid formed in the reaction, by the presence of which the change is accelerated. This action of acetic acid scarcely comes into play when strong acids are employed.

The examination of the action of acids on the change of acetamide into acetic acid and ammonium salt has established the connection between equilibrium and velocity which is predicted by theory; but the reaction employed was not of a kind to give completely accurate values for the velocity of the change, since too many secondary reactions exert their influence on the primary process. Another reaction studied by Ostwald (*J. pr.* [2] 28, 449) lends itself better for this purpose. This is the decomposition of ethereal salts by water in the presence of acids. Aqueous solutions of methyl acetate (or of similar compounds) undergo only very slow decomposition at ordinary temperatures; if, however, an acid is present the process is greatly accelerated. The acid does not undergo a permanent change, since at the end of the reaction exactly the same quantity of acid is found as was present at the beginning. It is doubtless by its affinity for the methyl alcohol that the acid influences the rate of the change. It *predisposes* in the sense already explained, only the compound which the acid forms with the methyl alcohol cannot exist in the presence of the great excess of water. The chemical process is represented by the equation $CH_3COOCH_3 + H_2O = CH_3OH + CH_3COOH$. Two substances are required; but the quantity of water is so great that its change need not be taken into account. Equations (1) and (2) must therefore hold good. This conclusion is verified by experiment. Thus for example 10 c.c. of normal hydrochloric acid were mixed with 1 c.c. of methylacetate and diluted with water to 15 c.c. One c.c. of this solution required for neutralisation 13·33 c.c. of baryta. Owing to the decomposition of the methyl acetate the acidity increased; the results are given in the first table of next column. The numbers in the last line represent the results when the decomposition was completed.

In the third column, under x, is given the increase in the number of c.c. of baryta used to neutralise the acid; the values in this column are always proportional to the quantity of methyl-acetate decomposed. The last value 14·11 gives the quantity a in the equation

$$\log \frac{a}{a-x} = kt.$$

Calculating the expression $\log \frac{a}{a-x}$ (for simplicity's sake in ordinary logarithms), and dividing it by the time t, k (= the coefficient of velocity) is obtained; the value of k is given in the last column; it is nearly a constant.

		x	k
After 14 minutes	14·25	0·92	0·00209
34 „	15·47	2·14	0·00211
59 „	16·85	3·52	0·00212
89 „	18·24	4·91	0·00209
119 „	19·48	6·15	0·00209
159 „	20·92	7·59	0·00211
199 „	22·15	8·82	0·00214
239 „	23·10	9·77	0·00214
299 „	24·21	10·88	0·00214
399 „	25·46	12·13	0·00214
539 „	26·42	13·09	0·00213
∞	27·44	14·11	—

The same method was used for determining the velocity of decomposition of methylacetate by many other acids; the coefficients, referred to HCl = 1, are collected in the following table:—

Acid	I.	II.
Hydrochloric . .	1·00	1·00
Hydrobromic . .	0·98	0·99
Hydriodic . .	0·96	0·98
Nitric . . .	0·92	0·96
Chloric . . .	0·94	0·97
Sulphuric . . .	0·547	0·739
Methylsulphuric .	1·00	1·00
Ethylsulphuric . .	0·99	0·99
Propylsulphuric .	0·98	0·99
Isobutylsulphuric .	0·97	0·98
Isoamylsulphuric .	0·96	0·98
Ethylsulphonic . .	0·98	0·99
Isethionic . .	0·98	0·99
Benzenesulphonic .	0·99	0·99
Formic . . .	0·0131	0·115
Acetic . . .	0·00345	0·0587
Propionic . . .	0·00304	0·0551
Butyric . . .	0·00299	0·0551
Isobutyric . . .	0·00268	0·0518
Monochloracetic .	0·0430	0·208
Dichloracetic . .	0·2304	0·480
Trichloracetic . .	0·682	0·826
Lactic . . .	0·00901	0·0949
Hydroxyisobutyric .	0·00921	0·0960
Trichlorolactic . .	0·069	0·263
Pyruvic . . .	0·067	0·259
Oxalic . . .	0·1746	0·430
Malonic . . .	0·0287	0·169
Succinic . . .	0·00496	0·0704
Malic . . .	0·01181	0·1086
Tartaric . . .	[illegible]2296	0·1515
Racemic . . .	0·0[illegible]296	0·1515
Citric . . .	0·01[illegible]	0·1279

In the second column I have given the square roots of the velocities of reaction; these numbers ought to be proportional to the affinities, if

the determination of the affinities were free from the influence of all secondary reactions. Comparing these numbers with those already obtained, the same order of affinities appears, but in this case the values are more nearly equal. This agrees entirely with what had been expected; for it has been often emphasised that, owing to the presence of neutral salts, the statical methods make the strong acids appear too strong, and the weak acids appear too weak. The numbers found in the present case can therefore be justly considered as approaching nearer to the true coefficients of affinity than the previous values.

It is of special interest that a reaction such as the catalysis of methylacetate, which is only very remotely connected with the process of the formation of salts, is yet doubtlessly brought about by that very property of acids which produces the latter class of reactions. This leads to the conclusion that the numerical values of all reactions exhibited by acids as such depend on that one property which till now has been somewhat vaguely termed the *strength* of the

Acid	I.	II.	III.
Hydrochloric . .	1·00	1·00	1·00
Hydrobromic . .	1·114	1·05	0·99
Nitric . . .	1·000	1·00	0·96
Chloric . . .	1·035	1·02	0·97
Sulphuric . .	0·536	0·732	0·739
Ethylsulphuric .	1·000	1·00	0·99
Isethionic . .	0·918	0·96	0·99
Ethylsulphonic .	0·912	0·95	0·99
Benzenesulphonic .	1·044	1·02	0·99
Formic . . .	0·0153	0·124	0·115
Acetic . . .	0·00400	0·0632	0·0587
Isobutyric . .	0·00335	0·0579	0·0518
Monochloracetic .	0·0484	0·220	0·208
Dichloracetic . .	0·271	0·521	0·480
Trichloracetic .	0·754	0·868	0·826
Glycolic . .	0·01308	0·114	—
Lactic . .	0·01066	0·103	0·0949
Methylglycolic .	0·01815	0·135	—
Ethylglycolic . .	0·01372	0·117	—
Methyllactic . .	0·01390	0·118	—
Diglycolic . .	0·0267	0·163	—
Pyruvic . . .	0·0649	0·255	0·259
Glyceric . .	0·01715	0·131	—
Oxyisobutyric .	0·01062	0·103	0·0960
Oxalic . . .	0·1857	0·430	0·430
Malonic . . .	0·0308	0·175	0·169
Succinic . . .	0·0545	0·0738	0·0704
Pyrotartaric . .	0·0107	0·103	—
Malic . . .	0·0127	0·113	0·109
Citric . . .	0·0173	0·131	0·128
Phosphoric . . .	0·0621	0·249	—
Arsenic . . .	0·0481	0·219	—

acids. In order to verify this assumption Ostwald (*J. pr.* [2] 29, 385, [1884]) investigated another process which is not connected with the formation of salts, viz., the inversion of cane sugar. The reaction proceeds, as in the case of methylacetate, by the addition of water—$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$—without an apparent intervention of an acid. Yet it takes place only in the presence of acids. It is a catalytic reaction in the same sense as that already considered. As again only one substance, the sugar, undergoes change, the same equation holds good. As an example has already been given which shows that the process is represented by equations (1) and (2), the velocities of inversion are now given directly (*v.* table in last column).

In the second column are given the square roots of the velocities of inversion, in the third column the corresponding values for the catalytic change of methylacetate. The agreement is evidently sufficiently great to prove the identity of the causes which produce the inversion of cane sugar and the decomposition of methyl acetate. This agreement also forms the complete experimental verification of the assumption that there exist constants of specific activity, which numerically determine all the manifestations of affinity exerted by acids as such. The numbers found for methylacetate and for cane sugar represent these constants with great exactitude. The process of the inversion of cane sugar had been already used by Löwenthal and Lenssen (*J. pr.* 85, 321, 401) for the purpose of measuring constants of affinity. These chemists did not, however, deduce the constants of inversion from their experiments, although the theory of inversion had been established long before by Wilhelmy (*P.* 81, 413), nor did they give a proof of the fact that there are other chemical reactions which proceed according to a course analogous to that observed by them in the inversion of cane sugar.

Besides the chemical methods for the determination of the affinities of acids, there is yet another method which, by means of physical measurements, allows very accurate determination of these values to be made. It has been proved beyond doubt that the electrolytic conductivities of acids are closely connected with their chemical properties; so that this conductivity is proportional to the velocity of the reactions produced by the acids. As the electrolytic conductivity can easily be measured to a high degree of accuracy, we have here a method of much importance for the solution of the problems connected with affinity. The existence of this relation was first recognised and enunciated by W. Hittorf (*W.* 4, 391), who had, however, almost no measurements at his disposal. Arrhenius (*Bijh. K. Svensk. Vet. Ak. Hand.* 8, Nos. 13, 14 (1884)) developed a theory of the chemical changes among electrolytes, starting with the supposition that the power of conducting electrolytically and the power of participating in chemical reactions were identical.

This theory leads to equations which agree with those of Guldberg and Waage. Finally W. Ostwald has considerably increased the somewhat scanty material available for comparisons between the power of inducing chemical reactions and electrolytic conductivity. He fully proved the proportionality between the velocity of the reactions induced by an acid and the electrolytic conductivity of the acid (*J. pr.* [2] 30, 93; *ib.* 30, 225 [1884]; *ib.* 31, 433; *ib.* 32, 300 [1885]). The following table shows this agreement. Under I. are given the electrolytic conductivities for normal solutions; under II. the velocities of inversion of cane sugar for semi-normal solutions; under III. the velocities of

decomposition of methylacetate for ½ normal solutions; all the numbers are referred to hydrochloric acid = 1.

Acid	I.	II.	III.
Hydrochloric	1·002	1·00	1·00
Hydrobromic	1·01	1·11	0·98
Hydriodic	1·01	—	0·96
Nitric	1·00	1·00	0·92
Sulphuric	0·65	0·73	0·74
Formic	0·0168	0·0153	0·0131
Acetic	0·00424	0·004	0·00345
Monochloracetic	0·049	0·0484	0·0430
Dichloracetic	0·253	0·271	0·230
Trichloracetic	0·623	0·754	0·682
Glycolic	0·0134	0·0131	—
Methylglycolic	0·0176	0·0182	—
Ethylglycolic	0·0130	0·0137	—
Diglycolic	0·0258	0·0267	—
Propionic	0·00325	—	0·00304
Lactic	0·0104	0·0107	0·0090
β Oxypropionic	0·00606	0·0080	—
Glyceric	0·0157	0·0177	—
Pyruvic	0·0560	0·0649	0·0670
Butyric	0·00316	—	0·00300
Isobutyric	0·00311	0·00335	0·00268
Oxyisobutyric	0·0124	0·0106	0·0092
Oxalic	0·197	0·186	0·176
Malonic	0·0310	0·0308	0·0287
Succinic	0·00581	0·0055	0·0050
Malic	0·0134	0·0127	0·0118
Tartaric	0·0228	—	0·0230
Racemic	0·0228	—	0·0230
Pyrotartaric	0·0108	0·0107	—
Citric	0·0166	0·0173	0·0163
Phosphoric	0·0727	0·0621	—
Arsenic	0·0538	0·0481	—

The agreement of the numbers in the three columns is evident, and proves the truth of the assertion made above.

In order to understand the relation between conductivity and the power of taking part in chemical changes, we must go back to the theory of Clausius and Williamson. According to this theory the molecules of the electrolytic substances are continually interchanging their constituent atoms. These atomic exchanges generally take place to an equal amount in all directions; but when an electric current is passing they are so influenced that the electropositive or basic constituents go to the one side, and the electronegative or acid constituents to the other side, each constituent separating from the solution on one of the electrodes. This motion of the constituents occurs to a greater extent the greater the difference of potential between the electrodes, *i.e.* the greater the electromotive force. The change proceeds according to Faraday's law of electrolysis, which states that the quantity of electricity passed is proportional to the equivalents of the parts of the molecules separated out. Put into a slightly different form, this means that each electrified atom, or group of atoms, conveys the same quantity of electricity *quite independently of its nature.*

Since the electric current only exerts a directive influence on the electrolyte, but does not itself induce the action, the conducting power of substances depends entirely on the power of interchanging their ions. But on that same power depends also the velocity of the chemical changes produced by these substances; hence it follows that the velocities of the reactions must be proportional to the conductivities of the reacting substances. The experimental proof of this proportionality is in itself an important point in favour of the theory of Williamson and Clausius. (In Faraday's works we also find views which agree in the chief points with those explained above.) For the experimental details of the method the reader must be referred to the papers of Kohlrausch, Arrhenius, and Bouty. A short account of the conceptions and definitions used will, however, be given here, since the assumptions generally used in physics proper do not lend themselves well for our purpose.

Imagine a vessel having the form of a parallelopiped, the two parallel sides of which form the electrodes, and imagine the distance between the two to be equal to unit length. Into this vessel we imagine a quantity of the electrolyte to be placed, either by itself or in solution, such that its weight in grams is numerically equal to its molecular weight. Let us further suppose that the electromotive force between the two electrodes is unity; then the quantity of electricity passed through in unit time represents the molecular conductivity. Since equal quantities of electricity are conveyed by each electrolytic molecule, the total quantity of electricity passed is proportional to the number of double exchanges which take place in unit of time in one molecular weight of the substance

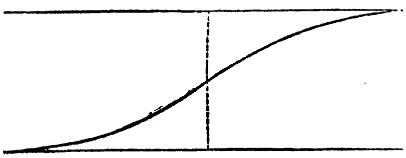
The electrolytic conductivity can be very easily and accurately determined. The possibility of solving a great many problems connected with the values of affinities is thus presented. W. Ostwald has specially investigated the influence of dilution, and has established the laws which hold for it. The simplest relations are found for the strong monobasic acids, hydrochloric, hydrobromic, hydriodic, nitric, chloric, and perchloric. For normal solutions all these acids have nearly the same conductivity, and this increases by about 10 per cent. to 12 per cent. with increasing dilution, gradually approaching a maximum value, which in the units used by Ostwald was equal to 90. Sulphocyanic and bromic acids approximate to the acids named above.

The other monobasic acids, which are weaker, and which therefore have smaller conductivities than those already mentioned, exhibit a greater change in conductivity with increasing dilution, the weaker they are, and they all do this according to the same law. This law states that *the dilutions at which two acids have the same molecular conductivity always bear the same ratio to each other.*

Thus, when measured in the units mentioned above, formic acid of the dilution 2—*i.e.* $H_2CO_2 = 46$ grams, in two litres of the solution—has the molecular conductivity 1·[illegible]6; butyric acid reaches the value 1·81 only at 32 litres dilution. On further dilution the following relation is manifested:—

Formic Acid		Butyric Acid	
Dilution	Conductivity	Dilution	Conductivity
4	2·47	64	2·56
8	3·43	128	3·50
16	4·80	256	5·01
32	6·63	512	7·02
64	9·18	1024	9·74
128	12·6	2048	13·4
256	17·0	4096	18·0
512	22·4	8192	23·8
1024	29·0	16384	31·5

Butyric acid and formic acid have always nearly the same molecular conductivity when the former is sixteen times as dilute as the latter. The same holds good for dilute solutions of all the monobasic acids. Plotting a curve, with the molecular conductivities as ordinates and the logarithms of the dilutions as abscissæ, we find it to have the shape indicated in the annexed figure. In this, the



logarithms are not referred to the base 10, but to the base 2, since in Ostwald's experiments the dilutions increase as the powers of two. They are the exponential powers, p, of the dilution v; $v = 2^p$.

The curve appears to be symmetrical about two lines at right angles to each other, and has a point of contrary flexure when the conductivity reaches the value 45. The equation to the curve can be approximately expressed—using the given units—by the empirical formula

$$\tan. m = \left(\frac{v}{v_0}\right)^{\cdot 4518}$$

where m is the molecular conductivity; v_0 the dilution (in litres per gram-equivalent) for which the conductivity is 45; and v any dilution for which the conductivity is to be calculated. The same curve holds for all acids if the abscissa v_0 is chosen properly. The value v_0 is characteristic for each acid. For the above-mentioned strong acids, it is found in high concentrations:—for iodic acid, at 2·8 litres approximately; for hypophosphorous acid, 8 litres; for dichloracetic acid, at 10 litres; for monochloracetic acid, between 400 and 500 litres; for formic acid, at about 1000; and for butyric acid, at about 10,000 litres.

The influence of the dilution on the relative affinities varies widely for the different acids, as has already been seen. It seemed therefore very doubtful whether much importance could be attached to these values as natural constants on which the action of the acid as such depends. In the law of dilution, as enunciated above, there has been found the proof that we are dealing with important and characteristic values, with values which do not alter with the nature of the reaction induced by the acid, and which are related to the dilution in a perfectly fixed manner. The general truth of this law for the case of chemical reactions has been separately proved by Ostwald (*J. pr.* [2] 31, 307). The values of affinities sought by men of science in the last century have thus been found by means of a method which had been even then indicated by the famous opposer of the old theory of affinity.

It has already been mentioned that the above law of dilution holds primarily for monobasic acids. Polybasic acids behave differently according to their constitution. Some dibasic acids, such as phosphorous, selenious, &c., in which the second hydrogen atom is of the nature of a weak acid (this is shown by the alkaline reaction of their normal salts), behave on dilution at first exactly like monobasic acids, the conductivity being referred to molecular and not to equivalent weights. Hence electrolysis of these solutions takes place at first according to the type H | HR″. It is only on reaching very great dilutions that the second hydrogen atom begins to participate in the reaction. Dibasic acids whose normal salts are neutral behave differently. It is true that they, too, conduct at first according to the type H | HR″; but the second hydrogen atom exerts its influence even in moderately dilute solutions. The conductivity increases much more rapidly than in the case of monobasic acids, and approaches a maximum which is double that observed for monobasic acids. Oxalic acid may be taken as a typical acid of this class. In the case of very strong dibasic acids, such as sulphuric acid, it is the last part of the phenomenon just described which becomes prominent. Even for a concentrated solution the molecular conductivity exceeds the maximum of monobasic acids, and rapidly approaches a value double that found with these acids. Hence conduction takes place from the beginning, for the most part, according to the type H_2 | R″.

Ostwald has recently (*J. pr.* [2] 32, 300) examined the conductivity of a number of acids, and has shown that the relations already stated hold in all cases. He has also established many relations between the conductivities of acids and their chemical constitution. This investigation opens up the possibility of drawing many inferences concerning the action of chemical forces. The following tables exhibit an abstract of the measurements of the molecular conductivities of various acids for the dilutions of 4, 32, and 256 litres:—

Acid	4 litres	32 litres	256 litres
Hydrochloric HCl .	80·9	87·0	89·2
Hydrobromic HBr .	83·4	87·9	89·6
Hydriodic HI .	83·2	89·6	89·7
Hydrofluoric HF .	6·54	13·14	30·3
Hydrocyanic HCN .	0·077	0·108	—
Sulphocyanic HSCN.	79·3	84·2	86·5
Sulphydric H_2S . .	—	0·214	—
Ferrocyanic $H_4Fe(CN)_6$	—	205·9	250·7

The acids which do not contain oxygen show great differences: HCl, HBr, HI, form a group of strong acids, while HF is much weaker; HCN can scarcely be called an acid; H_2S is slightly stronger; but if cyanogen combines with sulphur and hydrogen sulphocyanic acid is formed the strength of which approaches that of hydrochloric acid. Ferrocyanic acid is also a strong acid, though made up of the neutral iron cyanide and the weakly acid hydrogen cyanide.

Acid	4 litres	32 litres	256 litres
Nitric HNO_3 . .	80·4	86·3	88·4
Chloric $HClO_3$ . .	80·2	85·3	88·7
Perchloric $HClO_4$ . .	82·2	88·1	89·9
Bromic $HBrO_3$ . .	—	79·4	86·3
Iodic HIO_3 . .	50·6	72·3	81·8
Periodic H_5IO_6 . .	23·7	49·2	76·7

HNO_3, $HClO_3$, $HClO_4$ closely follow the halogen hydracids; $HBrO_3$ is weaker; HIO_3 is still weaker; and H_5IO_6 shows this decrease in strength to a marked extent. A similar relation is shown by the acids of phosphorus.

Acid	4 litres	32 litres	256 litres
Hypophosphorous H_3PO_2	37·91	62·1	77·84
Phosphorous H_3PO_3 .	34·29	56·96	74·54
Orthophosphoric H_3PO_4	17·00	31·41	61·8

Here too the acids become weaker as the amount of oxygen increases. The opposite relation is shown by the acids of sulphur and selenion.

Acid	4 litres	32 litres	256 litres
Sulphurous H_2SO_3 .	19·19	41·6	66·5
Sulphuric H_2SO_4 . .	96·4	116·3	150·6
Dithionic $H_2S_2O_6$ . .	—	166·4	178·0
Tetrathionic $H_2S_4O_6$.	—	170·6	181·5
Selenious H_2SeO_3 . .	9·74	21·73	45·11
Selenic H_2SeO_4 . .	103·2	127·0	157·9

The strength increases with increase of oxygen as well as with increase of sulphur.

As regards organic acids, the members of the acetic series are weak acids, and the strength decreases as we ascend in the homologous series.

Acid	4 litres	32 litres	256 litres
Formic HCO_2H .	2·47	6·63	17·0
Acetic CH_3CO_2H . .	0·755	2·12	5·64
Propionic $C_2H_5CO_2H$.	0·601	1·77	4·92
Butyric $C_3H_7CO_2H$.	0·604	1·81	5·01
Isobutyric $C_3H_7CO_2H$.	0·608	1·81	4·95
Valeric $C_4H_9CO_2H$.	0·615	1·87	5·16
Caproic $C_5H_{11}CO_2H$.	—	1·70	4·78

Appreciable differences are shown in the first three members only.

When chlorine, bromine, iodine, or cyanogen, is substituted for hydrogen, the acid character increases.

Acid	4 litres	32 litres	256 litres
Monochloracetic CH_2ClCO_2H	6·98	17·3	37·8
Dichloracetic $CHCl_2CO_2H$.	34·8	60·3	76·2
Trichloracetic CCl_3CO_2H .	65·9	75·0	79·1
Monobromacetic CH_2BrCO_2H	—	16·1	36·8
Cyanacetic CH_2CNCO_2H .	10·5	25·3	57·8
α-Bromopropionic $CH_3CHBrCO_2H$	7·87	17·6	36·2
β-Iodopropionic $CH_2ICH_2CO_2H$	1·534	4·385	11·6

The chlorinated acids are seen to increase in strength as the amount of chlorine increases but even trichloracetic acid does not reach the value for hydrochloric acid. The substitution of bromine, or cyanogen, for hydrogen acts in the same way as the substitution of chlorine; the action of cyanogen is much more marked than that of bromine. Introduction of the group OH for H in the fatty acids increases the strength of the acids, although not to so great an extent as is noticed in the preceding table.

Acid	4 litres	32 litres	256 litres
Glycolic CH_2OHCO_2H . . .	2·08	5·77	15·09
Glyoxylic $COH.CO_2H$ . . .	3·65	9·83	24·51
Lactic $CH_3CHOHCO_2H$ . .	1·94	5·49	14·42
β-Oxypropionic $CH_2OHCH_2CO_2H$.	0·896	2·63	7·18
Trichlorolactic $CCl_3CHOHCO_2H$.	11·0	27·7	54·8
Pyruvic CH_3COCO_2H . . .	9·05	22·1	43·8
Glyceric $CH_2OHCHOHCO_2H$.	2·46	6·87	17·9
α-Oxybutyric $C_2H_5CHOHCO_2H$.	1·44	3·99	10·08
β-Oxybutyric $CH_3CHOHCH_2CO_2H$	1·31	3·4	7·70
Oxyisobutyric $(CH_3)_2COHCO_2H$.	1·98	5·07	12·81
Methoxyacetic $CH_2OCH_3CO_2H$.	2·99	8·29	20·75
Ethoxyacetic $CH_2OC_2H_5CO_2H$.	2·40	6·94	17·98
Diglycolic $O(CH_2CO_2H)_2$ . .	5·00	13·78	33·58
Thiodiglycolic $S(CH_2CO_2H)_2$.	—	11·73	28·22

The influence of the relative positions of the OH groups appears to be of importance. In the cases of the isomeric lactic acids and the oxybutyric acids, that one is the strongest in which the OH is nearest the COOH group. Pyruvic and glyceric acids seem to obey the same law. The following members of the oxalic acid series have been investigated:

Acid	4 litres	32 litres	256 litres
Oxalic $(CO_2H)_2$	35·82	61·4	79·8
Malonic $CH_2(CO_2H)_2$ . . .	6·34	16·6	37·7
Succinic $C_2H_4(CO_2H)_2$ . . .	1·30	3·72	10·03
Methylmalonic $CHCH_3(CO_2H)_2$.	—	12·91	30·8
Pyrotartaric $C_2H_3CH_3(CO_2H)_2$.	2·29	5·74	13·19
Dimethylmalonic $C(CH_3)_2(CO_2H)_2$	—	12·14	29·59
Ethylmalonic $CH(C_2H_5)(CO_2H)_2$.	—	15·18	35·06
Suberic $C_6H_{12}(CO_2H)_2$ . . .	—	—	6·99
Sebacic $C_8H_{16}(CO_2H)_2$ . . .	—	—	6·6*
Malic $C_2H_3(OH)(CO_2H)_2$ . . .	2·97	8·63	22·28
Tartaric $C_2H_2(OH)_2(CO_2H)_2$ . .	5·05	13·68	33·15
Racemic $C_2H_2(OH)_2(CO_2H)_2$ . .	5·07	13·64	33·19
Saccharic $C_4H_4(OH)_4(CO_2H)_2$.	—	12·14	29·73
Mucic $C_4H_4(OH)_4(CO_2H)_2$ . .	—	—	16·39

* By extrapolation.

As the distance between the two carboxyls increases the dibasic acids become rapidly weaker; sebacic acid is scarcely stronger than the higher acids of the acetic series. Of the two isomerides, succinic acid and isosuccinic or methylmalonic acid, the latter has the carboxyls nearer together, and is therefore the stronger. Tartaric acid and racemic acid show no difference; hence the latter when in solution is not a compound of

right-handed and left-handed tartaric acid, as is the case in the crystalline form, but it is rather a mixture of the two.

The derivatives of benzoic acid are of special interest owing to the conditions under which isomerism occurs in this series. The following have been investigated:—

Acid	32 litres	256 litres
Benzoic $C_6H_5CO_2H$	—	9·95
Oxybenzoic [1:2] $C_6H_4OHCO_2H$	—	33·02
" [1:3] "	4·31	11·24
" [1:4] "	2·39	6·65
Nitrobenzoic [1:2] $C_6H_4NO_2CO_2H$	—	54·34
" [1:3] "	—	20·83
" [1:4] "	—	22·0*
Chlorobenzoic [1:2] $C_6H_4ClCO_2H$	—	32·54
" [1:3] "	—	15·13
" [1:4] "	—	12·7*
Bromobenzoic [1:2] $C_6H_4BrCO_2H$	—	38·89
" [1:3] "	—	14·8

* By extrapolation.

The substituting radicle always exerts most influence on the strength of the acids when it is in the ortho position. There is little difference between the meta and para positions. It is strange that para-oxybenzoic acid should be weaker than benzoic acid itself, as in all other cases the introduction of OH increases the strength of the acid. This points to the conclusion that the affinity-forces are of the nature of vector quantities, that is, that they are directed forces the resultants of which cannot be put as simply equal to the sums of the components. The other acids of the aromatic (or benzenoid) group for which measurements have been made are as follows:—

Acid	32 litres	256 litres
Amidobenzene sulphonic [1:3] $C_6H_4NH_2SO_3H$	4·55	16·13
Amidobenzene sulphonic [1:4] $C_6H_4NH_2SO_3H$	10·84	26·36
Mononitrophenol [1:2] $C_6H_4NO_2OH$	—	1·02
" [1:3] "	0·14	0·26
" [1:4] "	0·177	0·41
Dinitrophenol [1:2, 1:4] $C_6H_3(NO_2)_2OH$	—	10·95
Trinitrophenol [1:3:5] $C_6H_2(NO_2)_3OH$	—	79·7
Anisic $C_6H_4OCH_3CO_2H$	—	5·00
αToluic $C_6H_5CH_2CO_2H$	3·51	9·1
Phenylglycolic $C_6H_5CHOHCO_2H$	9·02	22·75
Phenoxyacetic $C_6H_5OCH_2CO_2H$	12·57	29·85
Phthalic [1:2] $C_6H_4(CO_2H)_2$	15·15	35·23
" [1:3] "	—	20·0
Nitrophthalic $C_6H_3(NO_2)(CO_2H)_2$	38·62	66·57
" "	29·22	57·50, 25·00

The introduction of NH_2 into benzene sulphonic acid, which is nearly as strong as hydrochloric acid, is accompanied by the production of a much weaker acid. The meta-acid is weaker than the para-acid. The three nitrophenols show the gradation ortho, para, meta, in the same way as the nitrobenzoic acids. The phenols rapidly increase in strength with the number of NO_2 groups they contain. Another point of interest is the difference exhibited by the isomerides anisic acid, phenylglycolic acid, and phenoxyacetic acid. Orthophthalic acid greatly exceeds metaphthalic acid in strength; while of its two nitro derivatives, the α compound, in which the NO_2 group is adjacent to the carboxyl, proves itself superior to the β derivative in which there is a greater distance between the NO_2 and the COOH groups. As regards the unsaturated acids, the following numbers show that they are the stronger the less hydrogen they contain.

Acid	4 litres	32 litres	256 litres
Acrylic $C_2H_3CO_2H$	1·25	3·46	9·20
Crotonic $C_3H_5CO_2H$	0·728	2·15	5·88
Fumaric } $C_2H_2CO_2H$	—	13·52	32·5
Maleic } $C_2H_2CO_2H$	17·46	39·15	65·49
Citraconic } $C_3H_4CO_2H$	9·56	24·05	49·67
Itaconic } $C_3H_4CO_2H$	1·92	5·33	14·66
Mesaconic } $C_3H_4CO_2H$	—	11·93	29·45
Hydrocinnammic $C_6H_5C_2H_4CO_2H$	—	2·26	6·08
Cinnammic $C_6H_5C_2H_2CO_2H$	—	—	7·56
Phenylpropiolic $C_6H_5C_2CO_2H$	—	27·66	52·0
Hydrosorbic $C_5H_9CO_2H$	—	2·29	6·29
Sorbic $C_5H_7CO_2H$	—	—	6·70
αBromocinnammic $C_6H_5C_2HBrCO_2H$	—	—	62·70
βBromocinnammic $C_6H_5C_2HBrCO_2H$	—	—	33·1
Meconic $C_5HO_2OH(CO_2H)_2$	—	102·1	141·5
Quinic $C_6H_7(OH)_4CO_2H$	—	7·81	19·92
Camphoric $C_8H_{14}C_2H_5CO_2H$	—	—	6·07

On comparing acrylic with propionic acid, crotonic with butyric acid, fumaric and maleic with succinic acid, and citraconic, itaconic, and mesaconic with pyrotartaric acid, it is evident that for each withdrawal of H_2 the acid becomes stronger. These relations become very conspicuous when we compare hydrocinnammic with cinnammic and phenylpropiolic acid, and hydrosorbic with sorbic acid. As regards the peculiarities of the dibasic unsaturated acids, they can only be just mentioned. Meconic acid, which stands by itself, is conspicuous by its great strength. It is the strongest of all acids which consist of carbon, oxygen, and hydrogen only, and it approaches very near to sulphuric acid. There is evidently some connexion between this property and the small amount of hydrogen this acid contains.

The introduction of amidogen and similar radicles makes the acids weaker.

Acid	8 litres	32 litres	256 litres
Amidoacetic $CH_2NH_2CO_2H$	0·236	0·257	0·32
Hippuric, $CH_2NH(C_6H_5CO)CO_2H$	—	6·68	17·38
Acetylamidoacetic $CH_2NH(CH_3CO)CO_2H$	—	6·88	17·76
Oxamic $CONH_2CO_2H$	21·07	35·88	62·26
Oxaluric $CO(NHCONH_2)CO_2H$	—	57·03	74·28
Parabanic $(CONH)_2CO$	43·35	48·23	53·96

The introduction of the NH_2 group into acetic acid is attended with a great reduction of the strength of the acid. This acid is considerably less weakened when one of the hydrogens in the NH_2 group is replaced by the negative radicle benzoyl or acetyl. Oxalic acid is also weakened by introducing the NH_2 group. On the other hand the introduction of the urea residue ($NHCONH_2$) into oxalic acid only slightly decreases the conductivity of the oxalic acid. Parabanic acid does not contain the carboxyl group, nor does it behave at all like an acid, since its conductivity increases but slightly with dilution.

The conditions of affinity among acids form the best-known part of the theory of affinity.

Our knowledge concerning the bases is much more scanty. From the fact that the relative affinities of acids are independent of the nature of the bases, we can infer that the relative affinities of the bases must also be independent of the nature of the acids (*J. pr.* [2] 16, 422). It is highly probable that the same laws hold for bases as for acids.

It must, however, be admitted that there is great lack of experimental data in this department. Some experiments of Menschutkin (*C. R.* 96, 256), who drew from them the conclusion that Berthollet's law of the influence of mass does not hold, prove only that under the conditions of the experiment the relative affinities of the bases compared—potash to aniline, to trimethylamine, and to ammonia, in alcoholic solutions—are very different. The same fact was proved by some thermo-chemical experiments of Berthelot.

Nor have many experiments been made by the kinetical method. Warder (*B.* 14, 1361) who first applied this method to bases, measured the velocity of decomposition of ethylic acetate. An investigation made by Reicher (Van't Hoff, *Dyn. chim.* 107) in connexion with Warder's work, showed that the velocity of the reaction is nearly the same for potash, soda, and baryta, the electrical conductivities being also nearly the same.

Ostwald (*J. pr.* [2] 33, 352) has recently investigated the electrical conductivities of some bases. The alkalis KOH, NaOH, LiOH, are strong bases; they have nearly the same conductivities. TlOH acts as an alkali. The conductivities of CaO_2H_2, SrO_2H_2, and BaO_2H_2, referred to masses *equivalent* to NaOH, &c., are the same as those of NaOH, &c.; the *molecular* conductivities of CaO_2H_2, &c., are, however, double those of NaOH, &c. Ammonia is a weak base; its conductivity is much influenced by dilution; the variations in the molecular conductivity follow the same law as was observed for acids. Substitution of H or H_2 in NH_3 by CH_3, C_2H_5, and other alkyl groups, increases the strength of the base; but $N(CH_3)_3$ and $N(C_2H_5)_3$ are weaker bases than $NH(CH_3)_2$ and $NH(C_2H_5)_2$. These bases all follow the same law of dilution. The non-volatile ammonium bases, *e.g.* NMe_4OH —and also the base $(C_2H_5)_3S(OH)_2$—exhibit conductivities nearly the same as those of the alkalis; guanidine is a little weaker, but belongs more to the ammonium bases than to the derivatives of ammonia.

In a memoir not yet published, Ostwald shows that these conclusions are confirmed by kinetical experiments on the saponification of ethylic acetate.

Besides the investigations which have led to numerical values for certain constants of affinity, there are numerous others from which such quantities cannot be deduced, because the reactions investigated were too complex. To this class belong principally the works of Berthelot and P. de St. Gilles on etherification, and the investigations of Menschutkin (collected in *A. Ch.* [5] 30, 31) on the same subject.

The importance of the first of these in chemical dynamics has already been emphasised. The latter have brought out interesting connections between the reactions observed and the chemical constitution of the acids used. The values obtained do not, however, lend themselves to the determination of coefficients of affinity; and the investigations themselves cannot therefore be considered here at greater length. The work of Horstmann (*B.* 12, 64), and of Dixon (*T.* 1884. 617), on incomplete combustion can likewise only be mentioned.

Little attention has as yet been directed to the investigation of the influence of temperature on the velocities of reactions, and on the constants of affinity. For the case of the inversion of cane sugar there are the investigations of Wilhelmy, Urech, and Spohr; for the velocity of etherification there are those of Berthelot and P. de St. Gilles, as well as those of Menschutkin. The whole question has been thoroughly investigated by Van't Hoff. By applying the dynamical theory of heat he finds that the equation for the relation between the temperature and the velocity of the reaction, k, must be of the form

$$\frac{d \log k}{d\tau} = \frac{A}{\tau^2} + B$$

where τ is the absolute temperature, and A and B are constants.

Van't Hoff has also shown that for several reactions the observed facts can be very well represented by such a formula. For details the book of Van't Hoff which has been mentioned must be consulted.

Berthelot and P. de St. Gilles have found that the chemical equilibrium of etherification is independent of the temperature within a wide range. Ostwald established the same generalisation for the relative affinities of various acids. Van't Hoff shows by the help of the dynamical theory of heat that this will occur when the reactions producing equilibrium do not give an appreciable thermal effect as their resultant. Moreover, when this is not the case, with a fall of temperature the equilibrium shifts in favour of that reaction which produces more heat than the reverse one (*l. c.* 167).

We have now arrived at the point where we must take up the problem concerning the relation between affinity and production of heat. As soon as it had been recognised that the thermal action accompanying a chemical reaction was the measure of the chemical *energy* used up therein, an attempt was made to apply this to the question of affinity.

In 1854, J. Thomsen enunciated the following laws (*P.* 92, 34). The magnitude of the force evolved in the formation of a compound is equal to the quantity of heat produced. When a compound is decomposed by another body the reason for this is that the stronger affinities satisfy themselves; hence decomposition must be accompanied by an evolution of force. Since chemical force when liberated under ordinary conditions generally manifests itself as an evolution of heat, it follows that '*every simple or complex effect of a purely chemical nature is accompanied by production of heat.*'

This deduction, plausible though it seems at first sight, is not correct. Heat does not measure forces but quantities of energy; hence the chemical production of heat does not tell us anything concerning the intensity of chemical forces: it is only the product of their (mean) value (if

we imagine them to be forces of attraction) into the space passed over by the atoms that is a quantity of energy, and as such is measurable by thermal methods. Since we know nothing about the spaces passed over by the atoms, and, moreover, cannot assume that the spaces are the same for all compounds, no conclusion regarding the chemical forces can be accurately drawn from measurements of the quantities of heat produced in chemical reactions.

To point out the old mistake would have been uncalled for, were it not that Berthelot has of late years enunciated an analogous erroneous 'law,' which he has defended with great warmth. It is the more necessary to submit this theory to criticism, as, owing to the great prestige which the renovator of this old mistake enjoys—a prestige he owes to his excellent experimental researches—the theory is surrounded as it were by a halo which has deterred many from closely examining it. Berthelot formulates his law as follows: '*Tout changement chimique accompli sans l'intervention d'une énergie étrangère tend vers la production du corps, ou du système de corps, qui dégage le plus de chaleur.*' And further: '*Toute réaction chimique susceptible d'être accomplie sans le concours d'un travail préliminaire et en dehors de l'intervention d'une énergie étrangère à celle des corps présents dans le système, se produit nécessairement, si elle dégage de la chaleur.*'

By a vague connexion with general dynamics, Berthelot calls this *the principle of maximum work.* He assumes it to follow as a natural consequence from the dynamical theory of heat. This view is erroneous. There is no such thing as a law according to which a dynamical system is in equilibrium when the greatest possible quantity of its potential energy has been changed into actual energy; but this would be the dynamical analogue of the so-called chemical law.

There does, however, exist a law in the dynamical theory of heat according to which a system is in equilibrium when it has attained to the maximum *entropy*. This function, which was first introduced by Clausius, is, like the energy of a system, entirely dependent on the condition of the system; it is defined by the equation, $dS = \frac{dQ}{T}$, where S stands for entropy, Q for a quantity of heat given to the body, and T for the absolute temperature. Horstmann (*A.* 170, 192), was the first to apply this law to chemical phenomena. The investigation has also been carried out very fully by Willard Gibbs. Unfortunately, the law is of very limited application. The integration can only be accomplished if the substances experimented with are perfect gases: Horstmann has shown that the law of entropy then leads to the same result as is attained by applying Guldberg and Waage's law of the influence of mass. This law has thus been supplied from the theoretical side with a valuable confirmation.

As far as we can tell, the law of entropy does not generally lead to reactions which are quite completed on one side, but rather to conditions of chemical equilibrium between opposite processes. According to Van't Hoff (*l.c.* p. 153), these processes vary with the temperature, if they are accompanied by a positive or negative production of heat, and the law is that the equilibrium shifts the more in favour of the positive thermal production the lower is the temperature. It is, however, only at absolute zero that the reaction would take place in one direction only (if at this temperature chemical reactions are at all possible); and it is only for this limiting case that a law of maximum thermal effect would hold good.

This is all that the law of the maximum thermal effect really contains; it is a limiting case from which the actual conditions differ the more the higher is the temperature. Since the temperature at which ordinary chemical reactions occur is not very high, the reactions accompanied by production of heat preponderate. This had been already noticed by Thomsen, and the approximation to truth contained in the law we certainly owe to him.

What Berthelot has added refers to the cases of chemical equilibrium which have been established beyond doubt, and which, according to the principle of maximum work, ought not to occur; this law asserts that because one of two reciprocal reactions is attended with production of heat that one ought to take place exclusively. It is Berthelot's endeavour to reduce all reactions in which chemical equilibrium has been observed to cases of partial *dissociation*, wherein the masses of the reacting bodies do not act as wholes. To accomplish this, he is obliged to call reactions of a purely chemical nature, dissociations; for example, the decomposition of acid sodium sulphate in aqueous solution, a reaction brought about by the affinity between sulphuric acid and water. The whole explanation resolves itself into reasoning in a circle. It need scarcely be said that an explanation of this kind cannot account for the laws by which the chemical equilibrium, the velocity of chemical reactions, and the electrical conductivities of the reacting bodies, are connected.

There is no doubt that, with the possibility of a more general application of the laws of entropy to chemical reactions, thermochemical data will become important and fundamental means for the investigation of the relations of affinity. Moreover, there is little doubt that Bergmann's theory of affinity, revived in a thermochemical form, is not the solution of the problem, and that, in spite of its modern appearance, it can as little keep its ground against Berthollet's far-reaching views as it could in its older form.

Of all the great old-standing problems of chemistry, that of chemical affinity has been least developed. The general relations and laws given in this article refer only to a limited number of substances, and to a limited number of reactions; many parts of the question have not yet been investigated at all. Great and important progress has, however, been achieved by Berthollet's enunciation, and Guldberg and Waage's rational formulation of the law of active masses. It must, however, be admitted that there are some reactions which seem to contradict this law, and which cannot be explained by it when taken in its simple form. It is not necessary to reject the law on this account, as has been done by some. The actual conditions of each experiment we make

are so complex that we are not able to completely apply the law of the influence of mass. We must content ourselves with an approximation which does not always lie within the limits of experimental errors. The motions of the stars cannot yet be represented in strict accordance with the law of gravitation; yet the first approximation is sufficient to remove any doubts as to the validity of the law. The law of the influence of mass in its simple application is also only true to a sufficient approximation in those cases in which the effects considered are of great magnitude as compared with those neglected. (In connexion with *affinity* v. PHYSICAL METHODS; section *Optical.*) W. O.

AGAR-AGAR or *Bengal Isinglass.*

A vegetable gum obtained in China from seaweeds: *Eucheuma spinosum, sphærococcus lichenoides, spinosus,* and *tenax*. Transparent colourless strips, almost completely soluble in water: forms a large quantity of thick, tasteless, and odourless jelly. Dilute H_2SO_4 forms galactose, characterised by its conversion into galactonic acid by Br_2 and Ag_2O. This galactose is formed from a carbohydrate, $C_6H_{10}O_5$, present in the agar-agar (Bauer, *J. pr.* [2] 30, 367).

AGARICIC ACID

$C_{16}H_{30}O_5$aq. [139°] (J.); [145·7°] (F.). S. ·8 at 15°. Obtained, together with agaric resin, from the larch-fungus (*Boletus Laricis*) by extraction with dry ether (Fleury, *C. R.* 70, 53) or with 90 p.c. alcohol (Jahns, *Ar. Ph.* [3] 21, 221, 260).

Four-sided, silvery plates (from 90 p.c. alcohol at 50°) or prisms (from dry alcohol). V. sol. hot glacial HOAc or oil of turpentine, m. sol. chloroform or ether, v. sl. sol. benzene or cold water. Swells up and dissolves in boiling water but crystallises out again on cooling. Oxidised by HNO_3 to butyric and succinic acids.

Salts.—Amorphous, insoluble pps. The neutral salts, $M_2C_{16}H_{28}O_5$ lose H_2O at 120° becoming $M_2C_{16}H_{26}O_4$.—NH_4HA''.—Na_2A'' (at 120°).—K_2A''.—BaA''.—Ag_2A'': gelatinous pp. Hot alcoholic solutions give, with $AgNO_3$, a pp. of $Ag_2C_{16}H_{28}O_4$ (Jahns).

AGARICIN. The fly-agaric (*Agaricus albus*) yields to alcohol a non-nitrogenous crystalline powder having a sweet taste with bitter pungent after taste; slightly soluble in water, insoluble in ether; decomposed by boiling with dilute acids, or by contact with saliva, yielding a substance which exerts a slight reducing power on alkaline copper-solution (Schoonbroodt, *J.* 1864, 613). According to Jahns (*J.* 1883, 1400) it is identical with agaricic acid. H. W.

AGARIC RESIN v. AGARICIC ACID.

Red, amorphous, solid; melts at 89·7°; dissolves in absolute alcohol, ether, wood-spirit, and chloroform, but is insoluble in water, benzene, and CS_2; slightly bitter; dissolves in alkalis. Na salt precipitated by alcohol in flocks changing in 24 hours into long needles. Forms precipitates, mostly crystalline with metallic salts (Fleury, *C. R.* 70, 53). H. W.

AGARICUS. A genus of *Fungi.* Many fungi, especially the agarics, contain an amount of nitrogen exceeding that in peas and beans, varying from 3·19 p.c. to 7·26 p.c. (Schlossberger a. Döpping, *A.* 52, 106).

The solid tissue consists of cellulose. Agarics contain mannite and fermentable sugar, but no starch. Many agarics contain fumaric acid, sometimes associated with malic or citric acid.

Agaricus bulbosus and *A. integer* yield crystallisable hydrochlorides and platinochlorides of basic bodies (Thörner).

Agaricus ruber or *sanguineus* contains a colouring-matter, *r u b e r i n e,* soluble in water and in alcohol. It is rose-red by transmitted light, having two absorption bands in the green, but it exhibits strong blue fluorescence. Dilute HCl extracts an alkaloid, agarythrine, from the fungus; this alkaloid is converted by oxidising agents into a red substance, possibly ruberine (T. L. Phipson, *C. N.* 46, 199).

Agaricus integer, contains an acid, with following properties: white needles [70°], very soluble in ether, benzene, CS_2, $CHCl_3$, hot alcohol and acetic acid, insoluble in water, and cold alcohol and acetic acid.—A'_2Pb: insoluble white pp. [114°]. The alkaline salts are sparingly soluble in cold water, and the salts of the heavy metals, insoluble (Thörner, *B.* 12, 1635).

Agaricus atramentosus yields to boiling ether a dioxyquinone $C_{11}H_6O_2(OH)_2$. Dark brown metallic-shining laminæ, dissolving with yellow colour in alkalis, insoluble in water, ether, light petroleum, benzene, chloroform and CS_2. Sublimes with great difficulty in yellow microscopic tablets. It is reduced by boiling its alcoholic solution with zinc-dust, the resulting colourless liquid becoming yellow-green again on exposure to the air. The *ammonium salt* is a green crystalline powder, dissolving readily in water with violet colour, nearly insoluble in boiling absolute alcohol.—Ba *salt*: dingy flesh-coloured crystalline precipitate (Thörner, *B.* 11, 533). The *diacetyl derivative* $C_{15}H_{12}O_4 = C_{11}H_6O_2(OAc)_2$ forms small reddish yellow tablets.

Boletus Laricis contains besides agaricic acid and (25 p.c. of) agaric resin also 3 to 5 p.c. of a neutral body, which crystallises in needles, [272°], and may be sublimed (E. Jahns, *J.* 1883, 1400). H. W.

AGAVE. Well preserved juice of *Agave americana*, sp. gr. 1·046 at 15° was found by J. Boussingault (*A. Ch.* [4] 11, 447) to contain in 1000 parts: 26·45 levulose, 61·71 saccharose, 3·53 malic acid, 5·45 gum, 10·13 albumin, 0·06 ammonia, 6·21, inorganic salts, and 886·46 water. H. W.

AGE or **AXIN.** The fat of *Coccus Axin* growing in Mexico, consists of the glycerides of lauric and axinic acids (Hoppe, *J.* 1860, 324). H. W.

AGGREGATION, STATES OF.—In this article the differences between the properties of bodies in the solid, the liquid, and the gaseous, condition, are looked upon as due to differences in the state of aggregation of those small particles, of which, according to the molecular theory of the constitution of matter, all bodies are composed. According to this theory, our power of subdividing matter cannot be carried beyond a certain limit, whatever means—chemical, physical, or mechanical—we employ. In other words, the theory asserts that the largest quantity of a body which we cannot subdivide by any means in our power is of finite size; it is called the atom of the substance of which the body is composed. Each elementary body has its peculiar atom, and the union of atoms of different kinds forms the smallest quantity

which can exist of a compound substance; this, however, cannot, in accordance with the definition, be called an atom, since, by the nature of the case, it can be divided by chemical, and often even by physical, means. Though matter can be divided down into atoms by chemical means, yet we have reason to believe that when only physical processes are going on the sub-division of matter is not in general carried so far; and that just as in an army, though the unit is the individual soldier, yet for military purposes the soldiers forming a regiment always act together, so in matter, groups of atoms, called molecules, remain together for a considerable time. The molecule, however, is a very much less definite thing than the atom, and it must not be assumed without proof in each case that the term has always a definite meaning, or that there may not in the same body be molecules consisting of very different numbers of atoms. There is strong evidence, too, that, in some cases at any rate, the molecule does not always consist of the same atoms; the molecule after a time seems to break up and the constituent atoms find fresh partners. In some cases, however, such as those of the permanent gases, we have reason to believe that the number of molecules which consist of the same number—say N—of atoms, is enormously greater than the number of those consisting of any other number of atoms. If, however, we raise the temperature, then, in the case of some gases at any rate, dissociation sets in; that is, there are now a considerable number of molecules in which the number of atoms is less than N; this is shown by the abnormally small densities of such gases at high temperatures. On the other hand, the density of a vapour near its point of condensation is often abnormally great, as in the case of acetic, formic, and monochloracetic, acid; a part at any rate of this increase in density would seem to be due to the formation of molecules consisting of a greater number of atoms than those formed when the temperature was raised far above that of the point of condensation.

According to the molecular theory of matter, the difference between the molecular constitution of bodies in the solid, liquid, and gaseous, state is that in the solid state the molecules oscillate about a position of equilibrium and never get far from their original position in the body; in the liquid state the molecules are supposed not to oscillate about positions of equilibrium, but to be comparatively free to move in any direction; they cannot, however, move far without coming under the influence of other molecules, so that their courses are constantly being changed and do not bear any approximation to straight lines; in the gaseous state the molecules are so far apart that for the greater part of the time they are describing straight lines, the time during which they are under the influence of other molecules being an exceedingly small fraction of the whole time.

We must be careful to remember that there is no evidence that the molecules in the liquid or solid state consist of the same number of atoms as those of the same substance in the gaseous state; but that on the contrary it seems most probable that in the solid and liquid states the molecules are systems whose complexity is not only very different from the molecules in the gaseous state but that these molecular aggregations vary very much in complexity among themselves. These molecular aggregations are probably not permanent but are continually breaking up and their constituents changing partners; this breaking up and re-formation of the molecular aggregations would produce the same effect as the collisions between the molecules of a gas, that is, it would tend to equalise the distribution of momentum and energy, so that it would make the substance possess viscosity, and be able to conduct heat. In fact, the collision between two molecules of a gas is the formation and breaking up of a molecular aggregation, and the difference between this case and that of a solid or a liquid is that the ratio of the time the molecular aggregation lasts to the time which elapses between the formation of successive aggregations is much smaller in the case of the gas than in that of the liquid or solid. The simplest state of aggregation we can imagine is one where the molecule and the atom are identical, that is, where the molecule consists of only one atom; this case is realised by a monatomic gas such as mercury, and possibly by all gases when the temperature is sufficiently high. The properties of matter in this state have not been investigated with special regard to the differences between this and more complex states of aggregation; Schuster (*Pr.* 1885), however, has shown that the phenomena of the electric discharge through mercury vapour are quite different from those occurring in a gas whose molecules are polyatomic.

In the case of most elementary gases the molecules consist generally of two atoms, and this case has received by far the largest amount of attention both from the experimental and the theoretical point of view. The most important results of the kinetic theory of gases from the chemical point of view are:—first, Avogadro's law, which states that in equal volumes of all gases at the same temperature and pressure there are the same numbers of molecules. From this it follows at once that, as long as all the molecules consist of the same number of atoms, the ratio of the molecular weights of two gases is the same as the ratio of their densities. It must, however, be clearly understood that this result is only true for perfect gases, that is, for gases in which the pressure is produced entirely by the striking of the molecules against the sides of the vessel containing the gas, and not at all by the force between the molecules. If a gas obeys Boyle's law it is a perfect gas for this purpose, and we may apply Avogadro's law to it; this law is not, however, applicable when Boyle's law does not hold. If the departure from the law be slight, and if δp be the deviation of pressure from that given by Boyle's law, then the number of molecules in unit volume will equal the number in the same volume of a perfect gas at the same temperature and pressure multiplied by $\left\{1-\frac{\delta p}{p}\right\}$, where p is the pressure. This correction is quite appreciable in the case of all but the most permanent gases. Maxwell investigated the distribution of velocity among the molecules of a gas, and showed that when the

gas was in a steady state the molecules could not all be moving with the same velocity; he gave (*P.M.* [4] 19, 22) a formula which tells how many molecules there are whose velocities are between any assigned limits. We shall here, however, only give a few numbers calculated from that formula. To take the case of oxygen at 0°C., about $\frac{1}{2}$ the molecules are moving with velocities of between 300 and 600 metres per second, about $\frac{1}{4}$ between 300 and 100, only about $\frac{1}{100}$ with velocities less than 100 metres per second, and not $\frac{1}{1000}$ part with velocities greater than 1,200 metres per second. The velocities with which the molecules of the same gas are moving at different temperatures are proportional to the square roots of the absolute temperatures; thus the distribution of velocity among the molecules of oxygen at 273°C. would be got by multiplying by $\sqrt{2}$ all the velocities at 0°C. The velocities with which the molecules of different gases are moving at the same temperature are inversely proportional to the square roots of their molecular weights; thus, for example, the velocities of the hydrogen molecules are on a scale four times as great as that of the oxygen molecules.

We can estimate by the methods of the kinetic theory of gases (see Meyer, *Die Kinetische Theorie der Gase*) the number of molecules in a cubic centimetre of the gas, and the diameter of the molecule, if the molecule is looked on as a hard elastic sphere; or if the molecule be considered as a system, we can estimate the distance between two molecules when their paths become appreciably curved. We find as the result of such calculations that there are about 21 trillion molecules in a cubic centimetre of gas under the pressure of 760 mm. of mercury at 0°C; so that the mean distance between the molecules is between 3 and 4 millionths of a millimetre, or about $3\cdot5 \times 10^{-7}$ centimetres; the diameter of the molecule is probably between 1×10^{-7} centimetres and 3×10^{-9} centimetres, or between $\frac{1}{4}$ and $\frac{1}{105}$ of the mean distance between the molecules. Another quantity which it is important to know is the mean distance through which the molecule passes between two collisions; this is called the mean free path of the molecule, and it is inversely proportional to the density. For hydrogen at the pressure of 760 mm. of mercury the mean free path is about $1\cdot8 \times 10^{-5}$ centimetres; at the pressure of 1 mm. the free path is about $\frac{1}{71}$ of a millimetre; and at a pressure of a millionth of an atmosphere about 18 centimetres. When the free path is comparable with the dimensions of the vessel in which the gas is inclosed, the gas can exhibit phenomena of a different character from those shown when the free path is indefinitely small compared with the dimensions of the vessel. The radiometer exhibits effects of this kind, and Crookes has called a gas rarefied so much as to show rotation in a radiometer, matter in the fourth or ultra gaseous state. But this is using the word *state* in a different sense from that in which it is used in the phrases solid, liquid, and gaseous, states; for these states do not depend upon anything but the matter itself, while the ultra-gaseous state depends upon the ratio of the free path to the other lengths involved; if we increased all the lengths proportionately to the rarefaction, the gas would not show any of those properties which characterise the so-called ultra-gaseous state, while, on the other hand, if we experimented with small enough instruments we could get all the ultra-gaseous effects manifested by a gas at the atmospheric pressure.

The distribution of energy among the molecules is of much chemical interest. It seems, however, that in one respect the results of theory have been misinterpreted; it has been said that because iodine, for example, is dissociated at a temperature a little over 600°, and since in iodine at any temperature there are some molecules possessing the same amount of energy as those which are split up at 600°, that therefore these molecules ought to be split up, and if any substance were present capable of combining with free iodine the whole of the iodine would ultimately combine with this substance. Now although there are apparently no experiments which may be called secular to say whether or not this would ultimately happen, yet it is certain that it does not happen so quickly as theory would indicate, if every molecule which possessed the same kinetic energy as that possessed by the average molecule at 600° were straightway dissociated and entered into combination with the other substances present; there seems, however, to be no reason why this should be the case, for though one molecule at 0° may have the same energy as one at 600°, yet dissociation must depend upon the surrounding molecules as well as upon the molecule itself. Now the molecule at 600°, though it possesses at any instant the same energy as one at 0°, is yet surrounded by molecules which are moving very much faster than itself, and whose energy is much more nearly equal to its own, so that it is not so likely to lose its energy by collision with other molecules as the molecule at 0° which is surrounded by molecules with much less energy than itself. For this reason the tendency to dissociate will be very much greater at 600° than at 0°, and a molecule at the former temperature may dissociate while the latter may lose its energy before this can happen.

The distribution of energy affects the specific heat very much; so that if we know the value of the specific heat we can tell a good deal about the energy of the molecule, as the following theoretical investigation will show. Let us begin with the case of a gas the molecule of which is of any degree of complexity, measured by the number of degrees of freedom, p. There is a theorem due to Boltzmann which states that the mean energy corresponding to each degree of freedom is the same, so that the mean total energy of the molecule is $\frac{p}{3}$ times the mean energy due to the translatory motion of the centre of gravity. Though there is very strong evidence against the truth of the theorem in this form, and the mathematical proof of it is unsatisfactory, yet a very special case of it is probably true, viz. that if we have a molecule consisting of n atoms approximately symmetrically arranged (that is, if the distance between a particular pair of atoms is not always very much

less than the distances between the other pairs), then the ratio of the mean total kinetic energy of the molecule to the energy due to the translatory motion of its centre of gravity is proportional to n, the number of atoms in the molecule.

Let the ratio of the total kinetic energy to the translatory energy of the centre of gravity, which by the kinetic theory of gases is measured by θ the absolute temperature, be βn. Then the total kinetic energy in the gas $=\Sigma\beta n\theta = \beta N'\theta$, when N' is the number of atoms in the gas. If all the atoms be of the same mass, m, and the quantity of gas be the unit of mass, then $N'm = 1$, so that the total kinetic energy in the gas $=\frac{\beta\theta}{m}$, which, if β be the same for all elementary gases, is inversely proportional to the atomic weight of the gas. If the gas had been a compound such that each molecule consisted of a atoms of mass m, b of mass m', c of mass m'', and so on, then for unit mass of the gas,

$$\frac{N'(ma + m'b + m''c)}{(a+b+c)} = 1,$$

so that the energy in unit mass

$$= N'\beta\theta$$

$$= \frac{\beta\theta(a+b+c)}{ma + m'b + m''c}.$$

Now $a+b+c$ is the number of atoms in the molecule, and $ma + m'b + m''c$ is the mass of a molecule, so that the energy of unit mass

$$= \frac{\beta\theta(\text{number of atoms in the molecule})}{\text{mass of the molecule.}}$$

Let us first suppose that all the energy in the gas is kinetic, then the energy in unit mass of the gas at temperature θ is $\frac{\beta\theta}{m,}$ so that the specific heat is $\frac{\beta\theta}{m,}$ or the product of specific heat into the mass of an atom, which is called the atomic heat, is equal to β, and, as experiment shows, does not vary much from gas to gas. For a compound, we see from the expression given above for the energy, that the product of the specific heat into the mass of a molecule equals β(number of atoms in the molecule), so that for all perfect gases, simple or compound, the product of the specific heat into the mass of the molecule $= \beta$(number of atoms in the molecule). We may remark that with our assumptions the ratio of the specific heat at constant pressure to that at constant volume

$$= 1 + \frac{2}{3\beta}\left(1 + \frac{\delta p}{p}\right)\frac{1}{\text{number of atoms in the molecule,}}$$

when δp is the deviation of the pressure from that given by Boyle's law. The experimental results show that for most perfect gases, simple or compound, the molecular heats are constant, showing that β is constant for such gases, or that the whole kinetic energy is proportional to the product of the number of atoms in the molecule and the energy due to the translatory motion of the centre of gravity. There are, however, some simple gases, such as chlorine and bromine vapour, whose atomic heats are much higher than the value given by the above rule. These gases are, however, easily liquefied, and so when heat is applied, work is done in altering the molecular state as well as in raising the temperature; this will produce an effect equivalent to increasing β, and will therefore explain the large value of the atomic heat. We should expect a large value for this quantity too if the gas were dissociating. There are some compound gases, on the other hand, such as ammonia, ethylene, and marsh gas, whose molecular heats are too small to agree with the above rule, if we suppose that the number of different systems in the molecule is the same as the number of atoms indicated by the chemical formula of the gas. If, however, two or more atoms always remain close together, they will for our purpose count as one atom, as it is only when the molecules are approximately symmetrically arranged that we can assume that the total energy is proportional to the number of atoms. The total energy is proportional to the number of distinct systems; and if a group of atoms always remain close together they only count as one system, however many atoms there may be. If, for example, the atoms in a radicle always remain together, the radicle, for this purpose and in the formula for the ratio of the specific heats, will only count as one atom. We may therefore regard those compounds which have too small atomic heats, as consisting of but few separate systems, though there may be a great number of atoms in the molecule.

The determinations by Dulong and Petit and others of the specific heats of elementary bodies in the solid state show that for these bodies the atomic heat is approximately constant, while Kopp's experiments on the specific heats of compound solid bodies show that for many such solids the product of the mol. w. and the specific heat is proportional to the number of atoms in the molecule, just as for gases. The expression for the kinetic energy of unit mass of a solid will probably be of the same form as that which we found for a gas; for this only depends upon the assumptions that the absolute temperature is proportional to the mean energy due to the translatory motion of the centre of gravity of the molecules, and that the ratio of the mean total kinetic energy of the molecule to the mean energy due to the translatory motion of the centre of gravity is proportional to the number of atoms in the molecule. These assumptions will probably hold for the solid and liquid as well as for the gaseous state. We must remember that when heat is applied to a solid or liquid, work is done in altering the molecular configuration as well as in increasing the kinetic energy of the molecules. All solids and liquids appear to be able to get into a condition in which the specific heat does not alter with the temperature, and it is in this condition that the atomic heat is constant. Now if the specific heat is independent of the temperature, the work spent in altering the molecular configuration must bear a constant ratio to the work spent in increasing the kinetic energy; and if the atomic heat is constant this ratio must be the same for all substances; so that Dulong and Petit's experiments show that when heat is applied to a solid or liquid it is divided between the energy of molecular configuration and the mean kinetic energy, in the same proportion for all substances; and since for many substances, such as iodine, bromine, mercury, &c., the specific heat in the solid state is twice that in

the gaseous, it is equally divided between these two forms of energy, a result which purely dynamical considerations would also lead us to regard as the most probable one. The specific heats of liquids seem to be more irregular than those of either solids or gases, but the bodies for which this is the case are those whose melting and boiling points are comparatively close together, and we may suppose that the nature of the molecular configuration alters with each change in temperature, and this makes the specific heat abnormally large. The specific heats of those substances which exist in the fluid state through wide ranges of temperature seem to be the same in the solid and fluid states.

When the specific heat of a solid compound is much smaller than the number of atoms in it would lead us to expect, we may, just as in the case of a gas, conclude that two or more atoms always remain close together in the molecule. It is important to notice, however, that the specific heat cannot give us any information about what we may call the molecular aggregation of the solid or liquid, that is it affords no information as to whether the molecules are isolated or form groups, for if we suppose the molecules to unite and form more complex ones the atomic heat would remain the same as long as the energy was equally divided among the atoms or radicles forming the molecules.

Change of State.—Gaseous to Liquid.

By the application of great pressure accompanied when necessary by intense cold, all gases have been liquefied, and during this process they pass through all intermediate states, so that at some stage of the process it is impossible to tell whether the substance is a gas or a liquid. It is found that there is for each gas a temperature above which it cannot be liquefied by the application of the most intense pressure, so that at a temperature higher than this the substance can only exist as a gas. This temperature is called the critical temperature, and Andrews has proposed to call a substance at a temperature higher than its critical temperature a gas, and one which though in a gaseous condition is yet at a temperature lower than the critical temperature, a vapour. Van der Waals (*Continuität des Gasförmigen und flüssigen Zustandes*, 87), and Clausius (*W.* 9, 1880), have shown how to calculate the critical temperature from the difference between the pressure of the gas in any state and that given by Boyle's law.

We shall here confine ourselves to showing, by general reasoning, that a critical temperature must exist. When a body is in the liquid state the ratio of the work required to separate the particles to an infinite distance to the kinetic energy of the molecules must exceed a certain limit, for the substance will behave as a liquid or a gas according as the forces between the molecules are or are not able to change their kinetic energy appreciably in the interval from one collision to another. The molecules will change their kinetic energy appreciably if the ratio of the alteration in the mutual potential energy of the molecules to their initial kinetic energy is finite, but for this to be the case the ratio of the work required to separate the molecules to an infinite distance must be finite, so for a body to be in the liquid condition this ratio must exceed a certain quantity, say, R. Let V be the work required to separate one of the molecules from the remainder, and T the kinetic energy of the translatory motion which is proportional to the absolute temperature; then the substance will behave like a liquid if $\frac{V}{T}$ be greater than R, but like a gas if $\frac{V}{T}$ be less than this quantity. Now V cannot be greater than the work, V′, required to separate the molecules when they are quite close together, so that when $T > \frac{V'}{R}$ the substance will always behave like a gas. Now T is proportional to the absolute temperature, so that when the absolute temperature exceeds a certain value the substance will always behave like a gas, that is, it cannot be liquefied. This shows that there must be a 'critical temperature,' and it also shows that the critical temperature is proportional to the work required to separate the molecules; a measure of this will be the amount of heat required to convert the substance from a liquid into a gaseous state under infinite pressure. We can take as a practical measure the latent heat of the substance. The mean kinetic energy of the translatory motion equals the absolute temperature, so that if h be the latent heat, θ the critical temperature, NV' will be proportional to h, where N is the number of molecules in unit mass, and T is proportional to θ, so that since $\frac{V'}{T}$ is constant, we should expect to find that the critical temperature multiplied by the number of molecules in unit mass—or, what is proportional to it, the reciprocal of the molecular weight—ought to be related to the latent heat so that when one is great the other is great also. The following table will show that this condition is approximately fulfilled:—

Substance	Absolute critical temperature	Critical temperature divided by mol. w.	Latent heat
Alcohol C_2H_6O . .	510	11·1	209
Acetone C_3H_6O . .	505	8·7	140
Carbon disulphide CS_2 .	546	7·3	105
Benzene C_6H_6 . .	558	7·17	109
Methyl acetate $C_3H_6O_2$.	503	6·8	110
Ethyl formate $C_3H_6O_2$.	503	6·8	105
Sulphurous oxide SO_2 .	429	6·7	94
Ether $C_4H_{10}O$ . .	468	6·3	94
Ethyl acetate $C_4H_8O_2$.	513	5·83	105
Chloroform $CHCl_3$.	533	4·51	67
Carbon tetrachloride CCl_4	557	3·6	52

Passage from the Liquid to the Gaseous State.

Though it requires the application of pressure and cold to make a substance pass from the gaseous to the liquid state, yet the substance will always to a limited extent pass of itself from the liquid into the gaseous state. In the space over a liquid in the equilibrium condition

there is always a quantity of the vapour of the liquid, the quantity of vapour in unit volume depending only on the nature of the liquid and the temperature; in other words, the vapour exerts a definite pressure called the vapour pressure (often erroneously the vapour tension). If we have a quantity of liquid in a vessel furnished with a piston the liquid will evaporate until there is a certain quantity of vapour in each unit of volume above the liquid; if we depress the piston so that this volume diminishes by v then a quantity of vapour equal to that in volume v will condense; if the piston be raised again the vapour will be re-formed. In this way we can have a continual transference from the gaseous into the liquid state and back again. In this process, however, we have only matter in these two states and have no continuity of state from the gaseous to the liquid as we had in the process by which the permanent gases are liquefied. The vapour pressures of different liquids vary enormously; thus for sulphuric acid the vapour pressure is so small as to be almost inappreciable; for sulphuric acid, mixed with its own volume of water, it is about one-eighth of a mm. at 15°C.; for water at the same temperature it is about 12·6 mm.; for alcohol, 32 mm. The vapour pressure always increases as the temperature rises, but until the temperature reaches a certain value depending on the pressure, the liquid which evaporates is always that on the surface, and none of the liquid in the interior passes into the gaseous condition. When, however, the vapour pressure becomes greater than the pressure on the surface of the liquid, the bubbles of vapour which form on the sides will be at a pressure equal to or greater than the pressure in the surrounding fluid, and so will expand and be able to reach the top without condensing. When this takes place, *i.e.* when portions of the liquid not on the surface are converted into gas, the liquid is said to boil. The temperature of the boiling-point will increase with the pressure; it cannot, however, even by the application of an infinite pressure, be raised above the critical temperature of the substance. Bodies which have small vapour pressures at ordinary temperatures have high boiling-points; but it does not follow that because the vapour pressure of one substance is at some temperature greater than that of another its boiling-point will be lower; for example, at 15°C. the vapour pressure of carbon tetrachloride is greater than that of methyl alcohol, though its boiling point is higher. According to the molecular theory, some of the molecules manage to escape from the liquid, we may suppose because they are moving so fast as to be able to escape from the attraction of the other molecules; on the other hand, some of the molecules of the vapour strike the surface and get caught by the molecules of liquid. When things are in a state of equilibrium as many molecules escape from the liquid as are caught by it.

Although the vapour densities of many substances have been determined, few experiments seem to have been made on the rate of evaporation and condensation. The knowledge of these rates would very much increase our knowledge of the constitution of fluids.

The forces between the molecules in the liquid state must be sensible, otherwise we should not be able to spend work upon a liquid without increasing the kinetic energy, as we do when we convert water into steam at the same temperature. The latent heat may be taken as a measure of the potential energy lost by the transition from the gaseous to the liquid state. In a fluid the potential energy of the molecular configuration seems to depend only on the mean distance between the molecules; for the fluid resists anything tending to diminish its volume, but does not resist anything tending to change its shape. When the fluid is in such a condition that its specific heat is independent of the temperature then any increase in the kinetic energy must be accompanied by a proportionate increase in the potential energy of the molecular configuration. Now, if the forces between the molecules are large it will require a smaller increase in the distance between them to increase the potential energy by a given amount than if they were smaller; so that for a given increase in the kinetic energy, that is, a given rise in temperature, the increase in volume will be less when the forces between the molecules are great than when they are small, so that the coefficient of expansion will be small when the forces between the molecules are great, but when the forces between the molecules are great the fluid is incompressible and the product of the mol. w. and latent heat is large; so that we should expect a small coefficient of expansion, incompressibility, and large latent heat for equal volumes to go together, and we find by the following tables of these quantities that this seems to be the case.

Substance	Product of latent heat and mol. w.	Coefficient of expansion	Compressibility
Water, H_2O	11,088	·000065	4·51
Benzene, C_6H_6	8,502	·00138	
Acetone, C_3H_6O	8,120	·00172	
Chloroform, $CHCl_3$	7,906	·00140	
Carbon tetrachloride, CCl_4	7,904	·00140	
Ether $(C_2H_5)_2O$	6,956	·0021	10·8
Carbon bisulphide, CS_2	6,840	·00146	6·26

A peculiarity of water is that it is denser at 4°C. under atmospheric pressure than at any other temperature under the same pressure; we may perhaps suppose that this is due to something of the following kind. We know that when water freezes it expands and crystallises in the hexagonal system; now we may suppose that, before the water solidifies, molecular aggregations are formed which possess the same property as is possessed by the ice crystals, viz. that when the molecules are arranged in this way they occupy a greater volume than when arranged uniformly—the formation of these aggregations would tend to increase the volume and might be sufficient to more than counterbalance the diminution due to the nearer approach of those particles which do not form these aggregations.

Change of State from Solid to Liquid.

When the temperature of a solid is raised sufficiently high it begins to melt. There are two kinds of melting; in the one, as in the case of ice, if the heat is applied slowly the tempera-

ture remains constant until all the substance has passed from the solid into the liquid state In this case there is a definite melting-point. In the other case, of which an example is the melting of sealing-wax, the substance first begins to soften, then as more heat is applied it gets softer and softer, its temperature, however, increasing until when a certain temperature is reached the substance is liquid; in this case there is no definite melting-point, as the process is spread over a considerable range of temperature. This would seem to imply that the substances which melt in the second way are not perfectly homogeneous in structure, but contain molecular aggregations of various degrees of complexity, which get gradually split up as the temperature rises; while those substances which melt like ice have a more uniform constitution, so that any change of state takes place simultaneously through the molecules. This would obviously tend to make the transition more definite. This view is in accordance with the fact that crystalline bodies, which are generally regarded as being more uniform in structure than non-crystalline, all melt in the same way as ice. Sealing-wax in the state of transition is what is called a viscous body; so that on this view a viscous substance is regarded as a mixture of molecules some of which are in the same state as they are when the substance is liquid, and some are in the same state as they are when the substance is solid. A dynamical illustration will enable us to see how such a body might behave like a rigid body under the action of rapidly changing forces, and like a fluid under constant or slowly varying forces. Suppose we have a series of heavy spheres connected by strong springs placed upon a horizontal table, and that one end of this row of spheres is fastened to a peg which cannot sustain a tension greater than T without breaking; then if a steady pull, T, be exerted at the other end of the row of spheres the string will break, but if the tension at the end, instead of being steady, be periodic, and if the period of vibration be greater than the natural period of vibration of the spheres and springs, then if the number of spheres be great enough the string will not break, though a tension enormously greater than T is acting at the other end. This is quite a parallel case to that of the viscous fluid; the springs and spheres correspond to those molecules which are in the same condition as when the substance is solid, the string to those in the fluid condition.

The change of state from solid to liquid seems to be always accompanied by a change in volume, and when this is so the melting-point —as J. Thomson proved—must be altered by the application of pressure. Thomson showed that this followed from thermodynamical considerations; and that when the substance expanded on solidification, like ice, the melting-point was lowered by pressure, but when the substance contracted on solidification the melting-point was raised by pressure. The most important substances which expand on solidification are water, bismuth, antimony, and cast-iron; none of these crystallises in the regular system, so that we may suppose that the molecules are arranged unsymmetrically, that while some are nearer together than when in the liquid state, others are further apart, producing on the whole an increase of volume.

The specific heat of a body in the solid condition is in general less than when it is in the liquid, except for those substances whose melting and boiling-points are very far apart, when it seems to be about the same in the two states; if we know the specific heat of a substance in both the fluid and the solid state at all temperatures, we can find the amount of heat necessary to convert unit mass of the substance from the solid to the liquid state. For Clausius has proved that if λ be the latent heat at the temperature t, s_1 and s_2 the specific heats in the solid and liquid states respectively at the same temperature, then

$$\frac{d\lambda}{dt}+s_2-s_1=\frac{\lambda}{t}.$$

A similar equation will apply to the change from the liquid to the gaseous state. Some bodies, such as camphor and iodine, sublime, that is pass directly from the solid to the gaseous state, and as these bodies exhibit a definite vapour-pressure—they must also pass directly from the gaseous into the solid states.

In the solid and liquid states the molecule is probably a very much more complex thing than the gaseous molecule, it is probably also not nearly so definite. Maxwell, in the article 'Atom' in the *Encyclopædia Britannica*, shows how the hypothesis of groups of molecules of different degrees of stability would explain the residual effects of elasticity, and states that in his view a solid consists of groups of molecules, some of which are in different circumstances from others. J. J. T.

AGONIADIN $C_{10}H_{14}O_6$. A crystalline bitter substance occurring in Agoniada bark (from *Plumeria longifolia*), which is used in Brazil as a remedy for intermittent fever. Needles, very bitter, v. sl. sol. ether, v. sol. hot alcohol, and CS_2. Nearly insoluble in cold, easily soluble in boiling water. When boiled with sulphuric acid it yields a sugar (Peckolt, *Ar. Ph.* [2] 144, 34). H. W.

ALACREATINE $C_4H_9N_3O_2$ *i. e.* $NH_2.C(NH).NH.CHMe.CO_2H$ *a-guanido-propionic acid.* S. 8·3 at 15°. Formed by mixing conc. solutions of alanine and cyanamide, adding a little NH_3, and allowing the mixture to stand (Baumann, *A.* 167, 83). Small prisms, v. sl. sol. cold alcohol. At 180° it changes into its anhydride, alacreatinine. Boiling baryta-water forms alanine and urea, or its decomposition-products, CO_2 and NH_3. HgO oxidises it, forming guanidine.

Methyl-alacreatine $NH_2.C(NH).NMe.CHMe.CO_2H$. From a-methyl-amido-propionic acid, cyanamide, and a little NH_3 (Lindenberg, *J. pr.* [2] 12, 253). Mono-clinic prisms, sl. sol. cold water or alcohol.

ALACREATININE $C_4H_7N_3O$ aq. Formed by dehydration of alacreatine by the action of heat or dilute acids, crystallises from water in long prisms, which give off aq in dry air or at 100°. M. sol. alcohol, more soluble in water than alacreatine. With zinc chloride it forms crystalline scales $(C_4H_7N_3O)_2ZnCl_2$, S. 4·35 at 20°, v. sl. sol. alcohol (Baumann, *B.* 6, 1371).

ALANINE $C_3H_7NO_2$, *i.e.* $CH_3.CH(NH_2)CO_2H$ *a-amido-propionic acid.* Mol. w. 89. S. 2·2 at 17°; S. (cold alcohol of 80 p.c.) ·2.

Formation.—1. From ethylic a-chloropropionate and ammonia (Kolbe, *A.* 113, 220; Strecker, *A.* 75, 29).—2. From a-bromopropionic acid and alcoholic ammonia (Kekulé, *A.* 130, 18).

Preparation.—An aqueous solution of 2 pts. aldehyde-ammonia is mixed with aqueous hydrocyanic acid containing 2 pts. HCy; hydrochloric acid is added in excess; the mixture is evaporated to dryness over a water-bath; the residue is digested with a mixture of alcohol and ether, which leaves NH_4Cl undissolved (Strecker).

Properties.—Tufts of colourless needles or oblique rhombic prisms, having a nacreous lustre. Sublimes at 200°. V. sl. sol. cold alcohol, insol. ether. The aqueous solution has a sweet taste, does not affect vegetable colours and gives no precipitates with any of the ordinary reagents. Alanine is isomeric with urethane, lactamide, and sarcosine; distinguished from the two former by not melting below 100°, and from the last by its solubility in water and its behaviour to metallic oxides.

Reactions.—1. Not altered by boiling with dilute *acids* or with *alkalis.*—2. Fused with KOH, it gives off hydrogen and ammonia and forms cyanide and acetate of potassium.—3. Resolved by boiling its aqueous solution with PbO_2, into aldehyde, carbon dioxide, and ammonia; $C_3H_7NO_2 + O = C_2H_4O + CO_2 + NH_3$.—4. Decomposed in aqueous solution by *nitrous acid,* with evolution of nitrogen and formation of lactic acid. H. W.

ALANT CAMPHOR $C_{10}H_{16}O$. Occurs in elecampane root, and is obtained together with solid alantic anhydride by distilling with water. Liquid smelling like peppermint, boiling at 200°. Heated with P_2O_5, it yields a hydrocarbon $C_{10}H_{14}$ which boils at 175°, and is converted by oxidisation with chromic acid into terephthalic acid (Kallen). H. W.

ALANTIC ACID $C_{15}H_{22}O_3$ [91°].—Obtained from its anhydride (*v. sup.*). Slender needles (from alcohol). Dissolves sparingly in cold, more readily in boiling water, very easily in alcohol. The *barium salt* forms warty masses moderately soluble in water. The *silver salt* $AgC_{15}H_{21}O_3$ forms small scales having a silvery lustre (Kallen, *B.* 9, 155).

Alantic Anhydride $C_{15}H_{20}O_2$ [66°], (275°), crystallises from dilute alcohol in prismatic needles. Easily sublimable. Dissolves very sparingly in water, very easily in alcohol, ether, &c.—The *chloride* $C_{15}H_{21}O_2Cl$ [140°] formed by passing HCl-gas into a solution of alantic acid in absolute alcohol, crystallises in large rhombic tablets, melting, with evolution of HCl, at 140°. It unites with bases, forming salts which readily decompose, with separation of metallic chlorides. By excess of caustic alkali it is converted into dialantic acid, $C_{30}H_{42}O_5$ (?)—The *amide* $C_{15}H_{21}O_2.NH_2$ [210°], obtained by passing ammonia-gas into an alcoholic solution of the anhydride, forms small crystals, melting, with decomposition at 210°, slightly soluble in alcohol, resolved by potash into ammonia and alantic acid. H. W.

ALBUMEN *v.* PROTEÏDS.

ALCAMINES *v.* ALKAMINES.

ALCOGEL. A gelatinous compound of silicic acid with alcohol (*q. v.*).

ALCOHOL C_2H_6O or EtOH (*ethyl alcohol, aqua vitæ*). Mol. w. 46. (78·2°) at 762·7 mm. (R. Schiff); (78·3°) (Regnault); (78·4°) at 760 mm. (Kopp, *A.* 92, 9); (78·5°) (Perkin); (12·8°) at 20·9 mm.; (21°) at 41·3 mm. (Kahlbaum, *B.* 16, 2480). S.G. $\frac{15}{4}$ ·79367 (S.); $\frac{15}{15}$ ·79503 (P.); $\frac{25}{25}$ ·78820 (P.); $\frac{20}{4}$ ·8000 (Brühl). S.V. 62·18 (S.); 62·7 (Ramsay). V.D. 1·613 (for 1·591, Gay-Lussac). S.H. ·615 (Kopp); ·659 (20° to 78°) (Reis); ·6019 (16°–20°); ·6067 (16°–35°); ·6120 (16°–40·5°) (J. H. Schüller, *P. Ergbd.* 5, 116, 192). H. F. p. 58,470. H. F. v. 57,020 (*Th.* iv. 229). μ_β 1·3667 R_∞ 20·31 (B.). M.M. 2·78 (P.).

Name.—The term *alcohol* was used in the time of Libavius (1595) to denote a powder. Spirit dried over powdered potassic carbonate was called *spiritus alcolisatus.* Kopp (*Geschichte,* iv. 281) suggests that this term does not mean spirit that has been treated with the powder, but that it is a corruption of *spiritus alcalisatus,* or spirit that has been treated with alkali. Alcolised or alcoholised spirit was then shortened to alcohol.

Occurrence.—1. In fermented saccharine juices.—2. In putrid, and even in healthy, tissues, such as ox-brain (Béchamp, *C. R.* 89, 573).—3. In crude coal-tar benzene (about 2 parts per million) (O. N. Witt, *C. C.* 1878, 416).—4. In the fruits and juices of some living plants (Gutzeit, *A.* 177, 344).—5. In bread (Bolas, *C. N.* 27, 271).—6. In crude wood-spirit (V. Hemilian, *B.* 8, 661).—7. Together with acetone, in the urine of diabetic patients (Markownikoff, *B.* 9, 1441, 1603).

Formation.—1. By the decomposition of glucose under the influence of ferments (*v.* FERMENTATION): $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$. Levulose, maltose, and melitose also give alcohol on fermentation.—2. From olefiant gas by dissolving it in conc. H_2SO_4, diluting and distilling (Hennel, *P. M.* 1826, 240; Berthelot, *A. Ch.* [3] 43, 385): $C_2H_4 + HHSO_4 = C_2H_5SO_4H$

$$C_2H_5SO_4H + H_2O = C_2H_5OH + HSO_4H.$$

The absorption of ethylene is greatly facilitated by heating the H_2SO_4 to 100° or, better still, 170° (Goriainow a. Butlerow, A. 169, 147).—3. By reduction of acetic anhydride (Linnemann, *A.* 148, 249), acetyl chloride (Saytzeff, *J. pr.* [2] 3, 76), or aldehyde, by means of sodium-amalgam.—4. By heating ether at 170° with water slightly acidulated with H_2SO_4 (Erlenmeyer a. Tscheppe, *Z.* [2] 4, 343).

Preparation.—When aqueous solutions of grape-sugar are fermented by yeast, 95 p.c. of the sugar splits up into alcohol and carbonic acid, but 4 p.c. goes to form succinic acid and glycerin, while 1 p.c. is used by the yeast as food. Small quantities of *n*-propyl, iso-butyl, and the two iso-amyl alcohols, $Me_2CH.CH_2.CH_2OH$ and $MeEtCH.CH_2OH$, are also formed. The mixture of these four alcohols is known as fusel oil. According to Rabuteau (*C. R.* 87, 500), potato spirit contains also iso-propyl, *n*-butyl, and secondary amyl alcohols.

The liquid to be fermented must contain nitrogenous matter and some inorganic salts to serve as food for the yeast; grape-juice, or a mixture of water with germinating barley (malt), to which a mash of potatoes may be added, are

the liquids usually employed. Diastase, an unorganised ferment in malt, converts the starch of the potatoes into a sugar, maltose, which then undergoes alcoholic fermentation.

When any of these alcoholic liquids are distilled the first portions of the distillate are rich in alcohol. By repeated rectification 'rectified spirit' containing 91 p.c. of alcohol may be got. Fusel oil may be removed by adding to the spirit about ·7 of its weight of coarsely powdered charcoal, leaving the mixture to stand for several days, and stirring repeatedly, then decanting and distilling. Animal or blood charcoal may also be used.

Absolute Alcohol.—The last traces of water may be removed by repeated rectification over freshly heated K_2CO_3, CaO, BaO, $CuSO_4$, or $CaCl_2$. The best way is to digest strong spirit with quick lime at 40° for two hours, and then, on distilling, to reject the first and last portions (Mendeléeff, *Z.* 1865, 260). If the spirit contain more than 5 p.c. of water a second treatment with lime will be necessary (Erlenmeyer, *A.* 160, 249). If dry baryta be used to complete the drying, as soon as the alcohol is absolute it will become yellow, dissolving a little BaO (Berthelot, *J.* 1862, 392).

References.—C. Bullock, *Ph.* [3] 4, 891; J. L. Smith, *Am. Ch.*, 5 120; Dittmar a. Stewart, *C. N.* 33, 53; Friedel a. Crafts, *A. Ch.* [4] 9, 5.

Properties.—A transparent, colourless, mobile, liquid. It has a characteristic odour and burning taste. When undiluted it acts as an inflammatory poison. It solidifies at −130·5° (Wroblewsky a. Olszewsky, *M.* 4, 338). Very hygroscopic. Miscible with water. Burns with a pale flame. Snow (1 pt.) mixed with alcohol (2 pts.) produces a freezing mixture (−20°, *Bn.* 1, 237).

Alcohol dissolves fats, oils, resins, alkaloids and most organic substances. It dissolves $CaCl_2$ and $SrCl_2$ but not $BaCl_2$; $Ca(NO_3)_2$ but not $Sr(NO_3)_2$ and $Ba(NO_3)_2$; LiCl but not KCl and NaCl. It does not dissolve carbonates or sulphates. It dissolves I, Br, P, and S.

The critical point of alcohol is 234·6° at 48,900 mm. At this point 1 g. occupies 3·5 c.c. (Ramsay a. Young, *Pr.* 38, 329). Alcohol vapour in contact with liquid acquires its normal density, 23, at 50° (R. a. Y.).

When alcohol is mixed with water contraction takes place and heat is evolved. The maximum contraction occurs when 49·8 vols. water and 53·9 vols. alcohol at 0° produce 100 vols. of mixture instead of 103·7 vols. This corresponds to a possible compound, EtOH 3aq (Mendeléeff, *Z.* 1865, 262).

The greatest difference between the observed specific heats of solutions of alcohol and the values calculated on the assumption of mere mixture occurs in a solution containing about 80 p.c. of alcohol by weight, corresponding to the formula EtOH 6aq. The greatest difference between the observed and calculated boiling-points and between observed and calculated capillarity also occurs in the same mixture, but the maximum deviation from calculated (or mean) compressibility is exhibited by a solution containing 40 p.c. of alcohol by weight (Dupré a. Page, *Pr.* 17, 333; *P. M.* [4] 38, 158). The maximum rate of transpiration through capillary tubes is exhibited by the solution EtOH 3aq (Graham, *A.* 123, 102).

Detection of Water in Alcohol.—1. $CuSO_4$ ought not to turn blue (Cassoria).—2. Benzene ought not to form a cloudiness, due to water-drops (Gorgeu, *C. R.* 30, 691).—3. Wet alcohol produces a pp. of BaO when added to a solution of BaO in absolute alcohol (Berthelot, *A. Ch.* [3] 46, 180).—4. If alcohol be added to a mixture of anthraquinone (·001 g.) with a little sodium amalgam, a green coloration indicates absence of water, otherwise a red colour is produced (Claus, *B.* 10, 927).

The following table gives the percentages of absolute alcohol, determined by Tralles:

Volumes per cent.	Weights per cent.	Specific gravity at 15·56°	Volumes per cent.	Weights per cent.	Specific gravity at 15·56°
0	0	1·0000	51	43·47	·9315
1	0·80	·9976	52	44·42	·9295
2	1·60	·9961	53	45·36	·9275
3	2·40	·9947	54	46·32	·9254
4	3·20	·9933	55	47·29	·9234
5	4·00	·9919	56	48·26	·9213
6	4·81	·9906	57	49·23	·9192
7	5·62	·9893	58	50·21	·9170
8	6·43	·9881	59	51·20	·9148
9	7·24	·9869	60	52·20	·9126
10	8·05	·9857	61	53·20	·9104
11	8·87	·9845	62	54·21	·9082
12	9·69	·9834	63	55·21	·9059
13	10·51	·9823	64	56·22	·9036
14	11·33	·9812	65	57·24	·9013
15	12·15	·9802	66	58·27	·8989
16	12·98	·9791	67	59·32	·8965
17	13·80	·9781	68	60·38	·8941
18	14·63	·9771	69	61·42	·8917
19	15·46	·9761	70	62·50	·8892
20	16·28	·9751	71	63·58	·8867
21	17·11	·9741	72	64·66	·8842
22	17·95	·9731	73	65·74	·8817
23	18·78	·9720	74	66·83	·8791
24	19·62	·9710	75	67·93	·8765
25	20·46	·9700	76	69·05	·8739
26	21·30	·9689	77	70·18	·8712
27	22·14	·9679	78	71·31	·8685
28	22·99	·9668	79	72·45	·8658
29	23·84	·9657	80	73·59	·8631
30	24·69	·9646	81	74·74	·8603
31	25·55	·9634	82	75·91	·8575
32	26·41	·9622	83	77·09	·8547
33	27·27	·9609	84	78·29	·8518
34	28·13	·9596	85	79·50	·8488
35	28·99	·9583	86	80·71	·8458
36	29·86	·9570	87	81·94	·8428
37	30·74	·9556	88	83·19	·8397
38	31·62	·9541	89	84·46	·8365
39	32·50	·9526	90	85·75	·8332
40	33·39	·9510	91	87·09	·8299
41	34·28	[illegible]	92	88·37	·8265
42	35·18	·9478	93	89·71	·8230
43	36·08	·9461	94	91·07	·8194
44	36·99	·9444	95	92·46	·8157
45	37·90	·9127	96	93·89	·8118
46	38·82	·9109	97	95·34	·8077
47	39·75	·9391	98	96·81	·8034
48	40·66	·9373	99	98·39	·7988
49	41·59	·9354	100	100·00	·7939
50	42·52	·9335			

The specific gravity of aqueous alcohol is given by Mendeléeff (*P.* 138, 103, 230) as follows:

Weight p.c. of absolute Alcohol	Specific Gravity, referred to Water at 4° at 0°	at 10°	at 20°	at 30°
0	·99988	·99975	·99831	·99579
5	·99135	·99113	·98945	·98680
10	·98493	·98409	·98195	·97892
15	·97995	·97816	·97527	·97142
20	·97566	·97263	·96877	·96413
25	·97115	·96672	·96185	·95628
30	·96540	·95998	·95403	·94751
35	·95784	·95174	·94514	·93813
40	·94939	·94255	·93511	·92787
45	·93977	·93254	·92493	·91710
50	·92940	·92182	·91400	·90577
55	·91848	·91074	·90275	·89456
60	·90742	·89944	·89129	·88304
65	·89595	·88790	·87961	·87125
70	·88420	·87613	·86781	·85925
75	·87245	·86427	·85580	·84719
80	·86035	·85215	·84366	·83483
85	·84789	·83967	·83115	·82232
90	·83482	·82665	·81801	·80918
95	·82119	·81291	·80433	·79553
100	·80625	·79788	·78945	·78096

The following table is given by Fownes (*Manual*, 3rd ed. 591), the specific gravities being taken at 15·6° C.:

Percentage by Weight	Specific Gravity	Percentage by Weight	Specific Gravity	Percentage by Weight	Specific Gravity
0·5	0·9991	34	0·9511	68	0·8769
1	0·9981	35	0·9490	69	0·8745
2	0·9965	36	0·9470	70	0·8721
3	0·9947	37	0·9452	71	0·8696
4	0·9930	38	0·9434	72	0·8672
5	0·9914	39	0·9416	73	0·8649
6	0·9898	40	0·9396	74	0·8625
7	0·9884	41	0·9376	75	0·8603
8	0·9869	42	0·9356	76	0·8581
9	0·9855	43	0·9335	77	0·8557
10	0·9841	44	0·9314	78	0·8533
11	0·9828	45	0·9292	79	0·8508
12	0·9815	46	0·9270	80	0·8483
13	0·9802	47	0·9249	81	0·8459
14	0·9789	48	0·9228	82	0·8434
15	0·9778	49	0·9206	83	0·8408
16	0·9766	50	0·9184	84	0·8382
17	0·9753	51	0·9160	85	0·8357
18	0·9741	52	0·9135	86	0·8331
19	0·9728	53	0·9113	87	0·8305
20	0·9716	54	0·9090	88	0·8279
21	0·9704	55	0·9069	89	0·8254
22	0·9691	56	0·9047	90	0·8228
23	0·9678	57	0·9025	91	0·8199
24	0·9665	58	0·9[illegible]01	92	0·8172
25	0·9652	59	[illegible]·8979	93	0·8145
26	0·9638	60	0·8956	94	0·8118
27	0·9623	61	0·8932	95	0·8089
28	0·9609	62	0·8908	96	0·8061
29	0·9593	63	0·8886	97	0·8031
30	0·9578	64	0·8863	98	0·8001
31	0·9560	65	0·8840	99	0·7969
32	0·9544	66	0·8816	100	0·7938
33	0·9528	67	0·8793		

Proof spirit was a term originally intended to denote spirit that was just strong enough to ignite gunpowder when burnt upon it, but it was defined by law in the reign of George III. to be spirit 'such as shall at the temperature of 51° F. weigh exactly twelve-thirteenth parts of an equal amount of distilled water.' It has, therefore, S.G. ·920 at 15·6° C., and contains 49·24 pts. alcohol to 50·76 pts. water by weight, or 100 vols. alcohol to 81·82 vols. water.

Alcoholic Drinks.—*Beer* contains from 2 to 6 p.c. of alcohol; *hock* and *claret* from 8 to 10 p.c.; *port* and *sherry* from 15 to 20 p.c.; *gin*, *rum*, and *whisky* from 51 to 54 p.c.

Detection.—1. The liquid supposed to contain alcohol is repeatedly rectified, after drying with K_2CO_3. The alcohol is recognised by its boiling-point, and by converting it into ethyl iodide, and noting the boiling-point of the iodide (72°).—2. The suspected liquid is distilled and some of the distillate (8 c.c.) mixed with water (10 c.c.) and H_2SO_4 (5 c.c.); some $KMnO_4Aq$, and after five minutes a solution of magenta, bleached by SO_2, are added. A red colour indicates that aldehyde had been formed by the oxidation of the alcohol. Acetone, formic acid and methyl alcohol do not show this reaction, so that it may be used to detect ethyl alcohol in wood spirit. Other primary alcohols behave more or less like ethyl alcohol (Riche a. Bardy, *C. R.* 82, 768).—3. An aqueous solution of alcohol warmed with KOH and iodine deposits iodoform. This 'iodoform reaction' is given also by aldehyde, acetone, *n*-propyl, *n*-butyl, sec. butyl, and octyl alcohols, by propionic and butyric aldehydes, by lactic, quinic, and meconic acids, by acetophenone, methylic butyrate, acetic ether, and oil of turpentine.

The 'iodoform reaction' is not given by methyl and amyl alcohols, by formic, acetic, butyric, valeric, oxalic, succinic, malic, tartaric, racemic, citric, pyrotartaric, suberic, sebacic, uric, mucic, isethionic, benzoic, salicylic, anisic, cinnamic, and picric acids, phenol, valeric aldehyde, benzoic aldehyde, glycol, glycerin, mannite, glycocoll, leucine, chloral, ethyl chloride, ethylene chloride and bromide, chloroform, tetrachloride of carbon, sulphide of carbon, toluene, and ether (Lieben, *A. Suppl.* 7, 226). Sugar and dextrin give a small amount of iodoform.

The formation of ethyl acetate and benzoate is also recommended as a test for alcohol.

Estimation.—The liquid is distilled and the S.G. of the distillate taken.

Detection of Fusel Oil.—1. The liquid is diluted with water until it contains about 12 p.c. alcohol; it is then shaken with chloroform. This extracts the amyl alcohol, which it leaves behind on evaporation; by warming with KOAc and H_2SO_4 this is converted into amyl acetate, smelling like pear-drops.—2. The alcohol is diluted until it forms a 50 p.c. solution. 100 c.c. are then shaken with 20 c.c. chloroform at 15° in a graduated cylinder. If the chloroform layer is 37·1 c.c. the alcohol is free from higher homologues, but if it occupy a larger volume, fusel oil is present. Thus 39·1 c.c. indicates 1 p.c. amyl alcohol (Röse, *B.* 19, R. 184).—3. The height to which the alcohol will rise in capillary tubes of known diameter is observed.

Pure alcohol rises higher than alcohol adulterated with fusel oil (J. Traube, *B.* 19, 892).

Reactions.—1. *Potassium* and *sodium* act upon alcohol, evolving hydrogen and forming EtOK and EtONa respectively.—2. *Phosphorus trichloride* forms EtCl, HCl, ethyl phosphite, and phosphorous acid (Béchamp, *C. R.* 40, 944): $6EtOH + 2PCl_3 = 3EtCl + 3HCl + Et_2PO_3 + H_3PO_3$. A smaller quantity of PCl_3 acts in the cold thus: $PCl_3 + HOEt = PCl_2(OEt) + HCl$ (Menschutkin, *A.* 139, 343).—3. PCl_5 reacts thus:

$$EtOH + PCl_5 = EtCl + ClH + PCl_3O.$$

4. P_2S_5 produces mercaptan:

$$5EtOH + P_2S_5 = 5EtSH + P_2O_5.$$

5. Alcohol coagulates *albumen*, and, partly on this account and partly by arresting the development of low organisms, it prevents the putrefaction of dead animal matter.—6. Vapour of alcohol passed through a *red hot tube* produces CO_2, water, hydrogen, CH_4, C_2H_4, naphthalene, and charcoal. If the tube be filled with pumice, benzene, phenol, and perhaps also aldehyde and acetic acid, are also formed (Berthelot, *A. Ch.* [3] 33, 295; *A.* 81, 108).—7. *Zinc dust* at 300°-350° forms ethylene and hydrogen: $C_2H_6O + Zn = ZnO + C_2H_4 + H_2$. Alcohol-vapour passed over zinc dust at a dull red heat forms CO, CH_4, and H_2 (Jahn, *M.* 1, 378).—8. Alcohol scarcely conducts an *electric current*, but when acidulated with 5 p.c. H_2SO_4 the current passes, hydrogen comes off at one pole and, at the other, aldehyde, ethyl formate sulphate and acetate, together with small quantities of acetal, and $CH_3.CH(OH)(OEt)$ are formed (Renard, *A. Ch.* [5] 17, 295). Alcohol containing a little potash produces hydrogen at the negative pole and aldehyde-resin at the positive pole (Connell).—9. Alcohol burns with a pale flame forming CO_2 and H_2O. Alcohol vapour undergoes rapid, but incomplete, combustion when mixed with air and exposed to finely divided *platinum*; acetic acid, aldehyde, formic acid, acetal, and acetic ether are formed. Hence a coil of red hot platinum wire will keep red hot if placed round the wick of a spirit lamp that is not burning (glow-lamp of Sir H. Davy).—10. Finely divided *rhodium*, *iridium*, and *ruthenium*, in presence of an alkali, decompose alcohol, with elimination of H and formation of an acetate (Deville a. Debray, *C. R.* 78, 1782).—11. *Oxygen* does not attack cold pure alcohol, but *ozone* forms acetic and formic acids (Boillot, *C. R.* 76, 1132).—12. *Chromic acid* mixture oxidises alcohol to aldehyde and acetic acid.—13. An *ammoniacal solution of* CuO at 180° attacks alcohol, forming acetic acid and Cu_2O (A. Letellier, *C. R.* 89, 1105).—14. $KMnO_4$ in acid, but not in alkaline, solution forms aldehyde and acetic acid (Chapman a. Smith, *C. J.* 20, 301). 15. Strong *nitric acid* acts violently, giving off copious red fumes containing nitrous ether, nitric oxide, CO_2, aldehyde, acetic and formic acids. If the action be moderated by making three layers of fuming HNO_3, water, and alcohol, and allowing them to mix slowly by diffusion, the following bodies are formed: aldehyde, acetic acid, glyoxal, glyoxylic acid, glycollic acid, and oxalic acid (Debus).—16. In presence of *urea*, *nitric acid* converts alcohol into ethyl nitrate (*q. v.*).—17. In presence of *mercuric nitrate*, *nitric acid* acts upon alcohol with production of fulminate of mercury (*q. v.*); in a similar way fulminate of silver may be made.

If mercury (1 pt.) be dissolved in HNO_3 (12 pts.) (S.G. 1·3) and the liquid left for some days till no more nitrous fumes appear and the liquid is colourless, and then alcohol (12 pts. of S.G. ·8) be added and the mixture be warmed, a pp. is produced which is not mercuric fulminate. It may be crystallised from diluted (4 vols.) HNO_3 (1 vol.). It is $C_2H_2Hg_3O_2(NO_3)_2$. At 120°-130° it explodes. It is insoluble in water, alcohol, and ether. *Potash* converts it into $C_2H_2Hg_3O_2(OH)_2$; while cold $K_2C_2O_4$ slowly converts it into the oxalate, $C_2H_2Hg_3O_2C_2O_4$, a body which is browned by sunlight. A mixture of HNO_3 and alcohol converts it into mercuric fulminate (Cowper, *C. J.* 39, 242; *v.* Gerhardt, *A.* 80, 101).—18. *Chlorine* is rapidly absorbed by alcohol, and in sunlight the liquid may even take fire. The ultimate product is chloral alcoholate, $CCl_3.CH(OEt)(OH)$, but this is probably the result of a long series of reactions (v. CHLORAL). Besides chloral, there are formed HCl, aldehyde, acetal, acetic acid, EtCl and other chlorinated bodies.—19. *Bromine* forms HBr, water, EtBr, bromal, and bromal alcoholate (E. Hardy, *C. R.* 79, 806).—20. Dry *chlorine* passed into alcohol mixed with $K_2Cr_2O_7$ gives aldehyde, EtCl, acetyl chloride, and EtOAc (Godefroy, *Bl.* [2] 40, 168).—21. When alcohol is distilled with much water and *bleaching powder*, chloroform (*q. v.*) is formed. When bleaching powder (300 grms.) is mixed with absolute alcohol (67 grms.) in 10 minutes the mixture gets hot and alcohol distils over together with a green oil, which explodes when exposed to sunlight or heated, and among the products of the explosion are mono- and di-chloro-acetal (Schmitt a. Goldberg, *J. pr.* [2] 19, 393), aldehyde, and small quantities of chloroform (Goldberg, *J. pr.* [2] 24, 97).—22. *Hydric chloride* produces ethyl chloride:

$$EtOH + HCl = EtCl + H_2O.$$

But when excess of alcohol is used and the solution heated in a sealed tube at 240°, ether is also formed: $EtOH + ClEt = Et_2O + HCl$ (Reynoso, *A. Ch.* [3] 48, 385).—23. *Sulphuric acid* mixes with alcohol with evolution of heat and formation of hydrogen ethyl sulphate:

$$EtOH + H_2SO_4 = EtHSO_4 + H_2O.$$

About half the alcohol and H_2SO_4 take part in the reaction; when more dilute acid is used hydrogen ethyl sulphate is not formed until heat is applied. If a mixture of alcohol with an equal volume (or less) of H_2SO_4 be heated, a further reaction sets in at 120°-150°, ether and water distilling over; this is due to action of alcohol upon hydrogen ethyl sulphate (Williamson, *C. J.* 4, 106, 229; *v.* ETHER):

$$HEtSO_4 + EtOH = H_2SO_4 + EtOEt$$

When alcohol is heated with twice its volume (or more) of H_2SO_4 the mixture begins to blacken between 160°-180°, and then gives off ethylene, mixed with SO_2, acetic acid, acetic ether, CO_2, CO, ethyl sulphate, and formic acid. The main reaction is expressed by the equation $C_2H_6O = C_2H_4 + H_2O$ (compare Erlenmeyer, *A.* 162, 373).—24. Anhydrous *sulphuric acid*, SO_3, dissolves in alcohol forming di-ethyl sulphate, Et_2SO_4. Vapour of SO_3 passed into dry alcohol forms crystals of ethionic anhydride,

$C_2H_4{<}{SO_3 \atop SO_2}{>}O$, or 'carbyl sulphate,' together with ethionic, isethionic, and sulphuric acids, and $HEtSO_4$.—25. Heated with *sulphurous acid* at 200° it forms $HEtSO_4$, ether, H_2SO_4, mercaptan, and S (Pagliani, *J.* 1878, 518).—26. $ClSO_3H$ forms $EtHSO_4$ and other bodies (Baumstark, *A.* 140, 75).—27. When alcohol is dropped upon hot *zinc chloride* the greater part is decomposed in accordance with the equation:

$$2C_2H_6O = C_2H_4O + H_2 + C_2H_4 + H_2O.$$

Hydrogen, ethane, HCl, and polymerides of aldehyde are also formed (W. H. Greene, *C. R.* 86, 1140). When wet alcohol is heated with $ZnCl_2$ at 155°, ether is formed, as well as EtCl, basic zinc chloride being left.—28. *Phosphoric acid* mixed with alcohol forms some di-hydrogen ethyl phosphate, EtH_2PO_4. Alcohol heated with P_2O_5 forms HEt_2PO_4 and Et_3PO_4 (Carius, *A.* 137, 121).—29. Alcohol heated with B_2O_3 forms $EtBO_2$ and Et_3BO_3.—30. *Phosphorus sulpho-chloride*, $PSCl_3$, forms di-hydrogen ethyl thio-phosphate (Chevrier, *Z.* [2] 5, 413):

$$PSCl_3 + 3HOEt = PS(OH)_2(OEt) + 2EtCl + HCl.$$

31. *Chloride of sulphur*, S_2Cl_2, acts upon alcohol forming ethyl chloride, ethyl sulphite, and a small quality of mercaptan (Carius, *A.* 106, 316).—32. *Chloride of antimony* dissolves in alcohol; if the solution be heated to 150° the following reaction ensues (H. Schiff, *A. Suppl.* 5, 218):

$$SbCl_3 + 4EtOH = SbOCl + 2EtCl + Et_2O + 2H_2O.$$

33. Heated with *carbon tetrabromide* at 100° for 12 hours, bromoform is produced (Bolas a. Groves, *C. J.* [2] 9, 784): $CBr_4 + C_2H_6O = CHBr_3 + C_2H_4O + HBr$. Alcohol here acts as a reducing agent, as it does also in the next reaction.—34. Heated with a *di-azo salt*, nitrogen is evolved and the entire di-azo group displaced by hydrogen:

$$C_6H_5.N_2Cl + C_2H_6O = C_6H_5H + N_2 + HCl + C_2H_4O.$$

In some cases the di-azo group is displaced by ethoxyl.—35. Heated with *ammoniacal zinc chloride* at 260°, alcohol is converted into a mixture of mono-, di-, and tri-ethylamine; the yield of mixed bases amounts to 45 p.c. of the alcohol used (Merz a. Gasiorowski, *B.* 17, 637).—36. *Zinc acetate* heated with excess of alcohol at 100° is converted, in about 30 hours, into zinc ethyl acetate and zinc oxide (Kraut, *A.* 156, 323). 37. When *stannic chloride* is distilled with alcohol, ether and EtCl pass over at 140°-170°; afterwards a compound of EtCl with $SnCl_4$ (Kuhlmann, *A.* 33, 106, 192).—38. Crystallised *stannous chloride* distilled with alcohol yields ether, but no EtCl (Marchand); the same decomposition takes place in a sealed tube at 240°. Crystallised *chloride of manganese*, and *ferrous chloride* also etherify alcohol completely at 240°; the *chlorides of cadmium, nickel,* and *cobalt* partially (Reynoso, *A. Ch.* [2] 48, 385).—39. *Platinic chloride* (1 pt.) dissolved in alcohol (10 pts.) of S.G. ·82 and distilled to $\frac{1}{6}$, yields aldehyde, ethyl chloride, HCl, and the solution contains the so-called inflammable chloride of platinum $C_2H_4PtCl_2$, which is left as a sticky mass when the liquid is evaporated (Zeise, *P.* 9, 632; 21, 498; 40, 249).—40. *Platinous chloride* boiled with alcohol forms a black explosive powder called *detonating platinum deposit*, C_2H_4PtO(?) (Zeise, *loc. cit.*).—41. *Mercuric chloride* is slowly reduced to calomel by alcohol.—42. Alcohol heated with *soda-lime*, air being excluded, is converted into sodic acetate, with evolution of hydrogen; at a higher temperature the sodic acetate breaks up into sodic carbonate and marsh-gas.—43. *Chloride of cyanogen* is readily absorbed by alcohol but does not decompose it immediately. After a few days, or more quickly at 60°, NH_4Cl separates, and the liquid then contains ethyl chloride, ethyl carbamate (or urethane), and ethyl carbonate (Wurtz, *A.* 79, 280).

Combinations.—Alcohol combines with many salts, acting like water of crystallisation.—$SbCl_3EtOH$ [67°] needles (from alcohol); resolved by heat into HCl, EtCl, Sb_2O_3, and $SbCl_3$. Soluble in ether and chloroform, but decomposed by water (W. C. Williams, *C. J.* 30, 463).—$AsCl_3EtOH$ (148°): liquid; fumes in the air; decomposed by water (Luynes, *A.* 116, 368).—$CaCl_2 4EtOH$: got by cooling an alcoholic solution of $CaCl_2$ with ice.—$CaCl_2 3EtOH$: got by evaporation of such solution over H_2SO_4 (Heindl, *M.* 2, 207).—$LiCl 4EtOH$ (Simon, *J. pr.* [2] 20, 376).—$MgCl_2 6EtOH$ (S.).—$Mg(NO_3)_2 6EtOH$ (Chodnew, *A.* 71, 256): a crystalline mass deposited from boiling solution.—$PtCl_4 2EtOH$ (Schützenberger, *J.* 1870, 388).—$SnCl_4 2EtOH$: crystals formed by evaporation over H_2SO_4 (Lewy, *C. R.* 21, 371; Robiquet, *J. Ph.* [3] 26, 161); heated with acids, this compound readily forms ethyl salts.—$TiCl_4EtOH$ [105°-110°] crystals; decomposed by water (Demarçay, *B.* 8, 75).

Alcoholates or Ethylates are formed by displacing the typical hydrogen by metals. They are decomposed by water:

$$MOEt + H_2O = HOEt + MOH.$$

Aluminium ethylate $Al(OEt)_3$ [130°] S.G.^{4} 1·147. Aluminium does not attack alcohol, but if iodine be present and the liquid be warmed, hydrogen is evolved and aluminium ethylate is formed (Gladstone a. Tribe, *Pr.* 30, 546): $2Al + 6HOEt = Al_2(OEt)_6 + 3H_2$. The reaction probably takes place in three stages:

$$3HOEt + Al_2I_6 = Al_2I_3(OEt)_3 + 3HI$$
$$Al_2(OEt)_3I_3 + 3HOEt = Al_2(OEt)_6 + 3HI$$
$$Al_2 + 6HI = Al_2I_6 + 3H_2.$$

Aluminium (4 g.), iodine (2 g.), and alcohol (40 c.c.), are heated in a flask with inverted condenser; when no more H comes off, the contents are distilled *in vacuo* at 300°. (Good yield (12 g.). G. a. T., *C. J.* 39, 2). When aluminium ethylate has been fused it remains liquid for a long time even at 70°. It is decomposed by water thus:

$$Al_2(OEt)_6 + 6H_2O = Al_2(OH)_6 + 6HOEt.$$

When distilled under atmospheric pressure it decomposes: $Al_2(OEt)_6 = Al_2O_3 + 3C_2H_4 + 3HOEt$, (G. a. T., *C. J.* 41, 5).

Barium ethylate $Ba(OEt)_2Aq$ (Berthelot, *A. Ch.* [3] 46, 180), $Ba(OEt)_2Ba(OH)_2$ (Destrem, *A. Ch.* [5] 27, 8, 22; *C. R.* 90, 1213). A granular pp. formed by boiling an alcoholic solution of BaO, or by heating alcohol with BaO in a digester at 150°. A white powder, turned yellow by oxidation. Converted by CO_2 into baric ethyl-carbonate. Destructive distillation gives C_2H_4, methane, H, and $BaCO_3$.

Calcium ethylate $Ca(OEt)_2$ resembles the barium compound.

Ferric ethylate $Fe_2(OEt)_6$ (?).—When the proper quantity of sodic ethylate is added to an

alcoholic solution of Fe_2Cl_6, all the chlorine is ppd. as NaCl, and the filtrate leaves, after evaporation, a black pasty mass, sol. alcohol, MeOH, ether, benzene, chloroform, or benzoline (Grimaux, *C. R.* 98, 105). A solution of ferric ethylate poured into water produces a solution of colloidal ferric hydroxide.

Potassium ethylate KOEt.—Similar in character to sodic ethylate.

Sodic ethylate NaOEt.—When sodium is dissolved in dry alcohol, H is evolved, and ultimately crystalline laminæ of NaOEt 2HOEt separate. If the solution be evaporated *in vacuo* at 20° needles of NaOEt 3HOEt are got (Forcrand, *Bl.* 40, 177). The alcohol of crystallisation may be driven off at 180°.

Reactions.—1. When mixed with *water* and distilled, alcohol passes over and NaOH is left.—2. Converted by EtI into ether (Williamson).—3. Forms ether when it acts on $EtNO_3$: but it acts like Na upon ethers of organic acids; thus it converts formic ether into CO and alcohol, oxalic ether into CO and carbonic ether, carbonic ether into $NaCO_3Et$ and Et_2O, benzoic ether into NaOBz and Et_2O, acetic ether into sodium aceto-acetic ether (Geuther).—4. CO combines with NaOEt at 100° forming sodic propionate. Carbonic oxide passed over a mixture of NaOEt and NaOAc at 205° produce *n*-butyric acid, di-ethyl-acetic acid, mesitylenic acid, an acid $C_{10}H_{14}O_2$ (250°-260°), and two ketones $C_9H_{18}O$ and $C_{15}H_{24}O$ (Geuther, *A.* 202, 305).—5. PCl_5 gives NaCl, $PO(OEt)_3$, and EtCl.—6. With *chloroform* it forms ortho-formic ether, $CH(OEt)_3$ (Williamson a. Kay, *C. J.* 7, 224).—7. *Chlorine* forms aldehyde and acetic acid (Maly, *Z.* [2] 5, 345).—8. *Bromine* forms bromal, EtBr, and acetic ether (Barth, *B.* 9, 1456).—9. *Chloro-acetic acid* forms sodium ethyl-glycolate (Heintz, *P.* 109, 301).—10. *Iodine* forms NaI, sodic formate, and iodoform.—11. *Iodoform* is reduced by NaOEt to methylene iodide.—12. *Nitrobenzene* is reduced to azoxybenzene, azobenzene, and aniline (Béchamp a. Saint-Pierre, *C. R.* 47, 24).

Thallium ethylate TlOEt. S.G. 3·5 to 3·685.—Formed by heating EtOH with thallium at 100° (Church), or by exposing thallium to the vapour of alcohol in a bell-jar full of oxygen (Lamy, *A. Ch.* [4] 3, 373). It may be solidified by great cold. It dissolves in dry alcohol or ether, but addition of a trace of water causes separation of thallous hydrate. TlOEt is slowly decomposed by $CHCl_3$ with separation of TlCl.

ALCOHOLS.—The term alcohol, originally limited to one substance, viz. spirit of wine, is now applied to a large number of compounds, many of which, in their external characters, exhibit but little resemblance to common alcohol. All alcohols are compounds of carbon, hydrogen, and oxygen, and are derived from hydrocarbons containing even numbers of hydrogen-atoms by substitution of one or more hydroxyl-groups, OH, for an equal number of hydrogen-atoms: thus from **propane** C_3H_8 or $CH_3.CH_2.CH_3$, are derived the three following alcohols:—

Propyl alcohol	C_3H_8O	$= C_3H_7(OH)$
Propylene alcohol	$C_3H_8O_2$	$= C_3H_6(OH)_2$
Propenyl alcohol or glycerin	$C_3H_8O_3$	$= C_3H_5(OH)_3$

Alcohols are classed as **monohydric**, **dihydric**, **trihydric**, &c., or generally as mono- and poly-hydric, according to the number of hydroxyl-groups which they contain.

An alcohol is **saturated** or **unsaturated** according to the nature of the hydrocarbon from which it is derived. Thus, all the three alcohols derived from propane C_3H_8, which is a saturated hydrocarbon, are themselves saturated molecules not capable of forming addition-compounds; but from the unsaturated hydrocarbon C_3H_6 is derived the unsaturated compound **allyl alcohol**, C_3H_6O or $C_3H_5(OH)$, which is capable of taking up 2 at. bromine and forming the compound $C_3H_6Br_2O$.

The replacement, partial or total, of the hydroxyl in an alcohol by Cl, Br, I, or F, gives rise to **haloid ethers**; thus:

From $C_3H_7(OH)$ are derived C_3H_7Cl, C_3H_7Br, &c.

From $C_3H_6(OH)_2$ are derived $C_3H_6Cl(OH)$, $C_3H_6Cl_2$, &c.

From $C_3H_5(OH)_3$ are derived $C_3H_5Cl(OH)_2$, $C_3H_5Cl_2(OH)$, $C_3H_5Cl_3$, &c. These substitutions are effected by treating the alcohols with the chlorides, bromides, and iodides of hydrogen and phosphorus, as in the formation of ethyl chloride from ethyl alcohol:

$$C_2H_5OH + HCl = H(OH) + C_2H_5Cl$$
$$3C_2H_5(OH) + PCl_3 = P(OH)_3 + 3C_2H_5Cl$$
$$3C_2H_5(OH) + POCl_3 = PO(OH)_3 + 3C_2H_5Cl.$$

Instead of the bromides and iodides of phosphorus, a mixture of phosphorus and bromine or iodine, in the proportions required to form them, are often used in these processes.—The haloid ethers are also formed in many instances by direct substitution of chlorine &c. for hydrogen in hydrocarbons.

The treatment of the alkyl chlorides, bromides, or iodides with aqueous caustic alkalis gives rise to a substitution opposite to that shown in the above equations, reconverting the ethers into alcohols; *e.g.* $C_2H_5Cl + KOH = KCl + C_2H_5(OH)$. A considerable portion of the alcohol thus formed is, however, converted by dehydration into the corresponding **olefin**: *e.g.* $C_3H_8O - H_2O = C_3H_6$. A better yield of alcohol is obtained by heating the haloid ether with moist silver oxide, which acts like a hydroxide AgOH; and a still better method is to convert the alcoholic chloride, &c. into an acetate by heating it with silver acetate or potassium acetate, and to boil the resulting alkyl acetate with caustic potash or soda;

$$C_2H_5Cl + KC_2H_3O_2 = KCl + C_2H_5.C_2H_3O_2$$
$$C_2H_5.C_2H_3O_2 + KOH = KC_2H_3O_2 + C_2H_5OH.$$

This reaction is of great importance in the preparation of some of the higher alcohols.

The replacement of the hydroxyl in an alcohol by the corresponding radicles, methoxyl OCH_3, ethoxyl OC_2H_5, &c.—or of the hydrogen in the OH by Me, Et, &c., gives rise to simple or mixed **alkyl oxides** or **ethers**: thus EtOH yields EtOK, EtOMe, and EtOEt; and ethylene alcohol $C_2H_4(OH)_2$ yields $C_2H_4(OH)(OEt)$ and $C_2H_4(OEt)_2$. These substitutions may be effected in various ways, the simplest being to replace a H-atom in the alcohol by K or Na, and act on the resulting compound with a haloid ether; *e.g.*

$$2C_2H_4(OH)_2 + Na_2 = 2C_2H_4(OH)(ONa) + H_2;$$
$$C_2H_4(OH)(ONa) + EtI = NaI + C_2H_4(OH)(OEt).$$

These oxides may be looked upon as anhydrides formed by elimination of one molecule of water

from two molecules of the same or different alcohols.

In the polyhydric alcohols, where the two hydroxyls occur in the same molecule, the elimination of water gives rise to another class of oxides; thus from ethylene alcohol $C_2H_4(OH)_2$ is derived ethylene oxide C_2H_4O.

The replacement of the hydrogen in an alcohol by acid radicles produces alkyl salts (also called *compound ethers or esters*); thus from methyl alcohol, MeOH, are derived a nitrate $MeONO_2$, an acetate MeOAc, an acid sulphate $Me.O.SO_3H$ and a normal sulphate $(MeO)_2SO_2$. These alkyl salts may also be derived from the corresponding acids by substitution of alkyl-radicles for hydrogen, being indeed related to the alcohols in the same manner as metallic salts to metallic hydroxides. They may also be looked upon as anhydrides formed by elimination of a molecule of water between one molecule of an alcohol and one molecule of an acid. By distillation with alkalis they are resolved into acid and alcohol; *e.g.*

$$EtOAc + KOH = KOAc + EtOH.$$

Monohydric Alcohols.

1. Series $C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$. Of this series the following members are at present known, each being derived from the corresponding paraffin C_nH_{2n+2} by substitution of OH for H: thus

Methyl Alcohol	$CH_3.OH$
Ethyl „	$C_2H_5.OH$
Propyl „	$C_3H_7.OH$
Butyl „	$C_4H_9.OH$
Amyl „	$C_5H_{11}.OH$
Hexyl „	$C_6H_{13}.OH$
Heptyl „	$C_7H_{15}.OH$
Octyl „	$C_8H_{17}.OH$
Ennyl or Nonyl Alcohol	$C_9H_{19}.OH$
Decyl Alcohol	$C_{10}H_{21}.OH$
Hendecyl „	$C_{11}H_{23}.OH$
Dodecyl „	$C_{12}H_{25}.OH$
Tetradecyl „	$C_{14}H_{29}.OH$
Hexadecyl or Cetyl Alcohol	$C_{16}H_{33}.OH$
Octadecyl Alcohol	$C_{18}H_{37}.OH$
Ceryl Alcohol	$C_{27}H_{55}.OH$
Melissyl or Myricyl Alcohol	$C_{30}H_{61}.OH$

The first and second of these alcohols do not admit of isomeric modifications; for supposing, as is most probable, that all the hydrogen-atoms in the paraffins methane CH_4 and ethane $CH_3.CH_3$ have the same value and are attached to their respective carbon-atoms in the same way, the result of the substitution of OH for H in them must be the same, whichever of the hydrogen-atoms is thus replaced. But in all the higher terms of the series the case is different. Thus in propane, $CH_3.CH_2.CH_3$, the substitution may take place either in one of the exterior groups CH_3, or in the middle group CH_2, giving rise to two alcohols of different structure, distinguished as primary and secondary, viz.

$$\underset{\text{Primary}}{CH_3.CH_2.CH_2OH} \quad . \quad \underset{\text{Secondary}}{CH_3.CHOH.CH_3}$$

In the primary alcohols the carbon-atom ... ; 40, 2 ... hydroxyl is connected immediately with alcohol ... other carbon atom, that namely called *detonating* ; but in the secondary alcohol (Zeise, *loc. cit.*).—41. ... other carbon-atoms, and these are the only forms of a 3-carbon alcohol of the series.

The 4-carbon alcohol of the series admits of a greater number of modifications. For in the first place, the hydrocarbon, butane, C_4H_{10}, from which it is derived, is itself susceptible of two forms, viz., *Normal butane* $CH_3.CH_2.CH_2.CH_3$ and *Isobutane* $CH_3.CH(CH_3)_2$; and further the first of these hydrocarbons is capable of yielding one primary and one secondary alcohol—these terms having the meanings above explained—while the second yields another primary alcohol, and likewise a tertiary alcohol, in which the C-atom joined to the hydroxyl is linked also to three other atoms of carbon. These four derivatives are represented by the following formulæ:—

Normal Primary $CH_3.CH_2.CH_2.CH_2OH$.
Isoprimary $(CH_3)_2CH.CH_2OH$.
Secondary $CH_3.CH(OH).CH_2(CH_3)$.
Tertiary $(CH_3)_2C(OH).CH_3$.

The higher alcohols of the series admit of a still larger number of isomeric modifications; but all these alcohols must be either primary, secondary, or tertiary; for the C-atom joined to the OH cannot be joined to a number of other carbon-atoms greater than three. In other words the replacement of an H-atom by the group OH must take place, either in a methyl-residue CH_3, a methylene-residue CH_2, or a methenyl residue CH, producing respectively a primary, secondary, or tertiary, alcohol.

A very convenient nomenclature for these isomeric alcohols has been introduced by Kolbe (*A.* 132, 102). Methyl alcohol is called carbinol and the higher alcohols named as its substitution-products, thus:

Carbinol or Methyl Alcohol CH_3OH.
Methyl-carbinol or Ethyl Alcohol $MeCH_2OH$.
Ethyl-carbinol or Propyl Alcohol $EtCH_2OH$.
Dimethyl-carbinol or Isopropyl Alcohol Me_2CHOH.
Propyl-carbinol or Butyl Alcohol $PrCH_2OH$.
Isopropyl-carbinol or Isobutyl Alcohol $PrCH_2OH$.
Methyl-ethyl-carbinol or Secondary Butyl Alcohol MeEtCHOH.
Trimethyl-carbinol or Tertiary Butyl Alcohol Me_3COH.

Primary, secondary, and tertiary alcohols are distinguished from one another by their products of oxidation. The primary alcohols of the series $C_nH_{2n+2}O$, containing the group CH_2OH, are converted by oxidation with chromic acid mixture, first into the corresponding aldehydes, by removal of H_2, or conversion of CH_2OH into CHO, and then by further oxidation into fatty acids $C_nH_{2n}O_2$; thus:

$$\underset{\text{Propyl Alcohol}}{CH_3.CH_2.CH_2OH} + O = H_2O + \underset{\text{Propionic Aldehyde}}{CH_3.CH_2.CHO}$$

$$CH_3.CH_2.CH_2OH + O_2 = H_2O + \underset{\text{Propionic acid}}{CH_3.CH_2.COOH}$$

A secondary alcohol on the other hand which contains two alcohol-radicles united by CHOH, is converted, by removal of H_2 from this group, into a ketone, *i.e.* a compound consisting of two alcohol-radicles united by the group CO, thus:

$$\underset{\text{Secondary Propyl Alcohol}}{CH_3.CHOH.CH_3} + O = H_2O + \underset{\text{Dimethyl Ketone}}{CH_3.CO.CH_3}$$

Conversely the aldehydes treated with nascent

hydrogen (action of sodium-amalgam) are converted into primary alcohols, and the ketones into secondary alcohols.

Tertiary alcohols do not yield by oxidation either aldehydes or ketones, or acids containing the same number of carbon-atoms as themselves, but are split up into bodies containing smaller numbers of carbon-atoms—tertiary butyl alcohol for example into formic and propionic acids:

$$(CH_3)_3COH + O_4 = CH_2O_2 + C_2H_4O_2 + H_2O.$$

The three classes of alcohols may also be distinguished by the following test:—A quantity of dry silver nitrite, mixed with an equal weight of dry sand, is introduced into a small distillation-flask fitted with a side-tube; the iodide of the alcohol under examination is then added; the mixture, after the reaction has begun, is distilled; and the distillate, received in a test-tube, is shaken up with potassium nitrite and potash-ley, and then acidulated with dilute sulphuric acid. If no coloration of the mass ensues, the alcohol-radicle present is a **tertiary**, whereas a red coloration indicates the presence of a **primary**, and a blue coloration that of a **secondary**, radicle. The reaction may be recognised with great distinctness with the use of not more than 0·3 to 0·5 grm. of the alcoholic iodide (Meyer a. Locher, *B.* 7, 1510). Secondary hexyl iodide does not give this test.

2. Series $C_nH_{2n}O$. The most important member of this series is **allyl alcohol** C_3H_6O, which is a primary alcohol, convertible by oxidation into acrylic aldehyde C_3H_4O, and acrylic acid $C_3H_4O_2$. They are unsaturated compounds capable of taking up 2 at. bromine, and forming the compounds $C_nH_{2n}Br_2O$.

3. Series $C_nH_{2n-2}O$. This series includes propargyl alcohol, di-allyl-carbinol, and the higher homologues of the latter.

4. Series $C_nH_{2n-6}O$. These alcohols are derived from the aromatic hydrocarbons, C_nH_{2n-6}, in the same manner as the fatty alcohols $C_nH_{2n+2}O$ from the paraffins. The lowest member, viz., **phenol** C_6H_6O or $C_6H_5(OH)$, which may be formed from benzene, C_6H_6, by oxidation with H_2O_2 or with nascent ozone (Leeds, *B.* 14, 96), is the only alcohol of the series containing 6 at. carbon. The higher terms admit of isomeric modifications: for all the homologues of benzene may be regarded as derived from benzene by substitution of one or more of its hydrogen atoms by alcohol radicles C_nH_{2n+1}, and the formation of an alcohol from such a hydrocarbon by substitution of OH for H may take place either in the benzene nucleus or in one of the substituting alcohol-radicles: thus from toluene $C_6H_5.CH_3$ may be obtained the two alcohols, $C_6H_5.CH_2OH$ (benzyl alcohol) and $C_6H_4(OH).CH_3$ (cresol), and the higher hydrocarbons of the series are capable of yielding a still greater number of metameric alcohols. The properties of the compounds thus formed differ considerably, according as the hydroxyl is introduced into the benzene nucleus, or into one of the associated alkyls. The compounds formed in the latter case—benzyl alcohol for example—are true alcohols analogous in all their reactions to those of the fatty series; but those in which the OH replaces a hydrogen-atom in the benzene nucleus (phenols) exhibit very different properties, the hydroxyl being much less easily displaced by other radicles (Cl, Br, &c.), *v.* PHENOLS).

5. Series $C_nH_{2n-8}O$. To this series belong **cinnamyl alcohol** $C_9H_{10}O$, **cholesterin** $C_{26}H_{44}O$, and allyl-phenol $C_9H_{10}O$.

DIHYDRIC ALCOHOLS.

These alcohols are derived from hydrocarbons by substitution of two HO-groups for two H-atoms, and may therefore be regarded as compounds of divalent alkyls with hydroxyl. Two series of them are known, viz., **glycols** derived from the fatty hydrocarbons, and **dihydric phenols** from the aromatic hydrocarbons.

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The lower glycols are described as GLYCOL, PROPYLENE GLYCOL, and *tri*-METHYLENE GLYCOL, but the higher members as *di*-OXY-BUTANE,-PENTANE, &c. Unsaturated glycols are described as *di*-OXY-BUTINENE, -HEXINENE, and -HEPTINENE. The chief di-hydric phenols are PYRO-CATECHIN, RESORCIN, and HYDROQUINONE. *Di*-OXY-NAPTHALENE and *di*-OXY-ANTHRACENE belong to this class.

TRIHYDRIC ALCOHOLS.

This class is represented by five fatty alcohols: GLYCERIN, and *tri*-OXY-BUTANE,-PENTANE,-HEXANE, and -HEXINENE. There are also several aromatic representatives, *e.g.* PYROGALLOL, PHLOROGLUCIN, and *tri*-OXY-NAPTHALENE.

TETRAHYDRIC ALCOHOLS.

Erythrite is the only fatty tetra-hydric alcohol known. **Tetra-oxy-benzene** and **tetra-oxy-tetra-phenyl-ethane**, and **tetra-oxy-tri-phenyl-methane** are aromatic tetra-hydric alcohols.

PENTAHYDRIC ALCOHOLS.

Pinite and **quercite** are the only ones known.

HEXAHYDRIC ALCOHOLS.

Mannite, dulcite, sorbite, perseite and **hexa-oxy-diphenyl** make a complete list.

Formation of Alcohols.—1. From haloid ethers as described above.—2. From aldehydes or ketones by reducing with sodium-amalgam.—3. From acid anhydrides by reduction with sodium-amalgam (Linnemann).—4. From primary amines by the action of nitrous acid; this reaction is, however, accompanied by an intra-molecular change in the case of all fatty amines except ethylamine and methylamine. As a result of this change *n*-propylamine gives rise to secondary as well as *n*-propyl alcohol.—5. *Secondary Alcohols* may be got by the action of zinc alkyls upon aldehydes:

$$RCHO + ZnEt_2 = R.CHEt.OZnEt$$

$$R.CHEt.OZnEt + H_2O =$$
$$R.CHEt.OH + EtH + ZnO$$

6. *Tertiary alcohols* can be formed, similarly, from zinc alkyls and acid chlorides:

$$CH_3.CO.Cl + ZnMe_2 = CH_3.CClMe.OZnMe$$

$$CH_3.CClMe.OZnMe + ZnMe_2 =$$
$$CH_3.CMe_2.OZnMe + ClZnMe$$

$$CH_3.CMe_2.OZnMe + H_2O =$$
$$CH_3.CMe_2OH + ZnO + CH_4$$

v. ZINC-METHYL.—7. From olefines, by dissolving them in H_2SO_4 and distilling the product with water: $Me_2C{:}CH_2 + H_2SO_4 = Me_3C.O.SO_3H$

$$Me_3C.O.SO_3H + H_2O = Me_3C.OH + H_2SO_4.$$

Just as: $C_2H_4 + H_2SO_4 = C_2H_5SO_4H$
$C_2H_5HSO_4 + H_2O = C_2H_5OH + H_2SO_4$.
By this reaction primary alcohols can be turned into secondary.—Thus conc. H_2SO_4 converts propyl alcohol into propylene, which is converted by the above treatment into iso-propyl alcohol.

Reactions of Alcohols.—Besides the general reactions mentioned above, the following are important:—1. Any reaction that might be expected to produce an alcohol of the form R.CH:CH.OH, produces an aldehyde, $R.CH_2.CHO$, instead (Erlenmeyer, *B.* 13, 309; 14, 320). Similarly an alcohol of the form R.CH:CR'.OH becomes a ketone, $R.CH_2.CR'O$.—2. On heating methyl, ethyl, butyl, octyl, and capryl alcohols with ammoniacal $ZnCl_2$ at 240°–280° a mixture of the mono-, di- and tri-alkylamines is got, the yield of which amounts to 50–75 p.c. of the alcohol (Merz a. Gasiorowski, *B.* 17, 623).—3. Tertiary alcohols differ from primary and secondary alcohols in not combining with *baryta* (Menschutkin, *J. R.* 10, 368).—4. Conc. HNO_3 converts tertiary alcohols into nitro-alkylenes, thus $(CH_3)_3COH$ becomes nitro-iso-butylene $C_4H_7NO_2$ (*Bn.* 1, 232).—5. The *boiling-points* of tertiary alcohols are lower than those of the isomeric secondary alcohols, and these again lower than those of the isomeric primary alcohols.—6. The alcohols $C_nH_{2n+2}O$ are decomposed by *zinc dust* at 300°–350° into olefine, C_nH_{2n}, and water. Methyl alcohol gives, however, CO and hydrogen (Jahn, *M.* 1, 378).—7. *Carbonic oxide* above 100° acts upon sodium alcoholates (RONa) mixed with sodium salts ($C_nH_{2n-1}O_2Na$) as follows:

$$RONa + CO + C_nH_{2n-1}O_2Na = CHNaO_2 + C_nH_{2n-2}RO_2Na$$

the elements of NaOH being abstracted so that R displaces H. A secondary reaction is

$$RONa + CO = RCO_2Na$$

(Geuther a. Froehlich; Looss; Poetsch, *A.* 218, 56). But CO does not act on a mixture of sodic phenylate and sodic acetate at 200° (Schroeder, *A.* 221, 35), or on one of sodic ethylate and sodic benzoate at 200°. On a mixture of sodic ethylate and sodic phenylacetate CO forms various acids including one (310°–320°) which may be phenyl-vinyl-butenyl acetic acid, $Ph.C(C_2H_3)(C_2H_2Et)CO_2H$. On a mixture of NaOEt and sodic cinnamate, carbonic oxide forms di-ethyl-cinnamic acid, $C_6H_5.CEt{:}CEt.CO_2H$ and di-butyl-cinnamic acid, $C_6H_5.C(C_4H_9){:}C(C_4H_9).CO_2H$. Both are oils.—8. Primary alcohols heated with *soda-lime* form acids and give off hydrogen thus: $RCH_2OH + KOH = RCO_2K + 2H_2$ (Dumas a. Stas, *A.* 35, 129). But at a higher temperature a second reaction occurs: $RCO_2K + KOH = RH + CO_3K_2$. If the hydrogen evolved be measured, some conclusion may be drawn as to the molecular weight of the alcohol; but the lower alcohols cannot give good results, as the hydrocarbons RH are gases. Myricyl alcohol gives off $\frac{12}{17}$ of the calculated hydrogen (C. Hell, *A.* 223, 269).—9. When an *alkyl carbonate* is heated with an alcohol, exchange of radicles occurs if the radicle of the alcohol contains more carbon atoms than that of the ether (Röse, *A.* 205, 240). But when an alcohol is heated with an *acetal*, exchange takes place only if the alcohol has the smaller radicle (Geuther, *A.* 218, 45). When an alcohol is boiled with a *simple ether* or with an ether of acetic or butyric acid with inverted condenser, no change occurs (G.).—10. If a small quantity of a *secondary* alcohol, other than isopropyl alcohol, be moistened with HNO_3 and then mixed with water and shaken with ether, on adding alcoholic KOH to the residue left after evaporating the ether, yellow prisms of a potassium alkyl nitrite separate (Chancel, *C. R.* 100, 601).—11. Benzoïn, isohydrobenzoïn, and pyrocatechin give, when their sodium compounds are treated with $ClCO_2Et$, neutral carbonates of the form $R''CO_3$, while resorcin, hydroquinone, and orcin give di-carbonates, $R''(CO_3Et)_2$ (M. Wallach, *A.* 226, 87).—12. On the *Rate of Etherification* of alcohols *v.* CHEMICAL CHANGE.—13. Fe_2Cl_6 gives a colour-reaction with all oxy-compounds whether aromatic or fatty, though in the latter case the reaction is faint and a nearly colourless solution of the reagent is required. Such a solution can be prepared by diluting two drops of 10 p.c. solution of Fe_2Cl_6 with 60 c.c. of water. If an excess of the substance to be tested is added to this solution a sulphur-yellow colour will be produced if a fatty alcohol, oxy-acid, or carbohydrate is present (Landwehr, *B.* 19, 2726).

ALDANE. A term proposed by Riban (*C. R.* 75, 98) to designate products formed by the union of two or more molecules of an aldehyde, with elimination of water—*e.g.* crotonic aldehyde $CH_3.CH{:}CH.CHO$ from aldehyde.

Di-aldane $C_8H_{14}O_3$ *i.e.*
$CH_3.CH(OH).CH_2.CH{:}CH.CH(OH).CH_2.CHO$
[130°]. S. (ether) ·87 at 22°. Formed by the condensation of aldol, $CH_3.CH(OH).CH_2.CHO$, under the influence of hydrochloric acid (Wurtz, *Bl.* [2] 24, 100; 28, 169). Crystallised from water. Sl. sol. cold water, v. e. sol. boiling alcohol. May be distilled *in vacuo.* It reduces silver solution. Aqueous NH_3 at 100° forms a crystalline base, $C_{16}H_{28}N_2O_3$, v. sol. water, alcohol or ether (Wurtz, *C. R.* 91, 1030). The aqueous solution of the base deposits, after some time, an amorphous isomeride.

Iso-di-aldane $C_8H_{14}O_3$ [114°]. Formed by heating aldol at 125° (W.) or by slow action of aqueous HCN upon aldol (Lobry de Bruyn, *Bl.* [2] 42, 161).

Di-aldanic acid $C_8H_{14}O_4$ *i.e.*
$CH_3.CH(OH).CH_2.CH{:}CH.CH(OH).CH_2.CO_2H$
[80°]. (198°) at 20 mm. Formed by treating an aqueous solution of di-aldane with Ag_2O or $KMnO_4$ (Wurtz, *C.R.* 83, 255, 1259). Monoclinic crystals. V.e. sol. alcohol or water, m. sol. ether. Salts:—KA' deliquescent crystals (from 98 p.c. alcohol).—NaA': plates (from alcohol).—BaA'_2: ppd. as powder by adding ether to an alcoholic solution.—CaA'_2 *x*aq: v. e. sol. water, but not deliquescent.—AgA': small laminæ (from boiling water); insol. alcohol.

Di-aldanic alcohol $C_8H_{16}O_3$ *i.e.*
$CH_3.CH(OH).CH_2.CH{:}CH.CH(OH).CH_2.CH_2OH$
[49°–53°]. (162°–165°) at 10 mm. Prepared by reducing di-aldane in aqueous solution with a large excess of (1 p.c.) sodium amalgam, the liquid being kept slightly acid with HCl. The liquid is neutralised and evaporated, freed from NaCl by alcohol, and the alcoholic solution distilled (Wurtz, *C. R.* 92, 1371). White, crystalline, deliquescent mass. V. e. sol. water and

alcohol; v. sol. ether. Ac_2O forms an acetate $C_8H_{14}Ac_2O_3$ (c. 159°) at 20 mm. Di-aldanic alcohol does not reduce ammoniacal $AgNO_3$.

Constitution.—The formation of a di-acetate seems inconsistent with the constitution assigned to di-aldanic alcohol. Di-aldane may be considered to be derived from di-aldol,

$CH_3.CH(OH).CH_2.CH(OH).CH_2.CH(OH).CH_2.CHO,$

by removal of H_2O. If this dehydration is to destroy two hydroxyls an anhydride must be formed:

$$CH_3.CH.CH_2.CH.CH_2.CH(OH).CH_2.CHO$$
$$\underbrace{O\qquad}$$

and the formulæ of dialdane derivatives must be altered accordingly.

ALDEHYDE (ACETIC) C_2H_4O, *i.e.* $CH_3.CHO$. Mol. w. 44. (21°). S.G. $\frac{0}{}$ ·800 (Kopp, *A.* 64, 214); $\frac{20}{4}$ ·7799 (Brühl); $\frac{10}{10}$ ·7951; $\frac{16}{16}$ ·7876 (Perkin, *C. J.* 45, 475). S.V. 56·6 (Ramsay). μ_β 1·3359. R_∞ 18·18 (B.). H.F.p. 48,740 (Thomsen); 46,000 (Berthelot). H.F.v. 47,870. M.M. 2·383 at 16·3°. V.D. 1·532 (for 1·520).

Occurrence.—In the first portions obtained by rectifying spirit that has been filtered through charcoal, where it is perhaps formed by oxidation in the charcoal (Krämer a. Pinner, *B.* 2, 403; 4, 787; Kekulé, *B.* 4, 718). The name *aldehyde* was invented by Liebig as a contraction of *alcohol dehydrogenatum.*

Formation.—1. In the oxidation of alcohol, either by slow combustion in contact with platinum black, or by the action of CrO_3, chlorine water, HNO_3, or a mixture of H_2SO_4 and MnO_2 (Liebig, *A.* 14, 133). Also by oxidation of acetic ether and other ethyl compounds (*e.g.* ethylamine, Carstanjen, *J. pr.* 89, 486), and by slow combustion of ether.—2. By action of $ZnCl_2$ on glycol: $C_2H_4(OH)_2 = H_2O + C_2H_4O$ (Wurtz, *A.* 108, 86).—3. From ethylene bromide and water at 160° (Carius, *A.* 131, 172) $C_2H_4Br_2 + H_2O = C_2H_4O + 2HBr$. From ethylene bromide and mercuric acetate (Linnemann, *A.* 143, 347).—4. From ethylene and CO_2 at 400° (Schützenberger, *Bl.* 31, 482).—5. From acetylene and aqueous $HgBr_2$ (Kutscheroff, *B.* 14, 1540).—6. By electrolysis of potassic lactate (Kolbe, *A.* 113, 244), of sugar solutions (H. T. Brown, *C. J.* 25, 578), or of alcohol containing H_2SO_4 or KOH (Jaillard, *C. R.* 58, 1203).—7. By dissolving acetylene in dilute H_2SO_4 (S.G. 1·35) and distilling the product with water (Lagermark a. Eltekoff, *B.* 10, 637).—8. By the dry distillation of a mixture of calcic acetate and calcic formate $Ca(CO_2CH_3)_2 + Ca(CO_2H)_2 = 2CaCO_3 + 2HCO.CH_3$ (Ritter, *A.* 97, 369).—9. By oxidation of ethylene with aqueous CrO_3 at 120° (Berthelot, *C. R.* 68, 334).—10. By reducing chloral with zinc and dilute H_2SO_4 (Personne, *C. R.* 71, 227).—11. Together with formic acid by heating lactic acid with dilute H_2SO_4 at 130°:

$$CH_3.CH(OH).CO_2H = CH_3.CHO + HCO_2H$$

(Erlenmeyer, *Z.* [2] 4, 343). Also, together with lactide, by the dry distillation of lactic acid.—12. Among the products of the action of H_2SO_4 and MnO_2 or $K_2Cr_2O_7$ upon albumen, fibrin, caseïn, gelatin (Guckelberger, *A.* 64, 46, 86), or gluten (Keller, *A.* 72, 31).—13. By heating acetal with glacial acetic acid at 180° for two days (Beilstein, *C. R.* 48, 1121).—14. By passing alcohol through a red-hot tube. From hemp oil in the same way (Hess, *P.* 38, 380). Aldehyde occurs among the products of the dry distillation of wood (Kane, *A.* 19, 288; Krämer, a. Grodzki, *B.* 9, 1921; Mabery, *Am.* 5, 258), and of sugar (Völckel, *A.* 87, 303).—15. By distilling α-di-alkylated-β-oxy-propionic acids:

$$CH_2.CH(OH).CEt_2.CO_2H = CH_3.CHO + CHEt_2CO_2H.$$

Preparation.—1. From the 'first runnings' in the rectification of fermented liquors.—2. Alcohol (3 pts. of S.G. ·842) and $K_2Cr_2O_7$ (3 pts.) are placed in a retort and conc. H_2SO_4 (4 pts.) is slowly run in. The heat evolved causes the aldehyde to distil off (W. a. R. Rodgers, *J. pr.* 40, 240). It is collected in dry ether, which is afterwards saturated with dry NH_3; aldehyde-ammonia separates in cubes, and this is distilled with H_2SO_4 (3 pts.) mixed with water (4 pts.), the receiver being cooled with ice and salt. The product is dried over $CaCl_2$ and rectified.

Properties.—Characteristic odour, miscible with water, but separated by $CaCl_2$ from solution. Neutral. Readily polymerised. Mixes with alcohol and ether. A mixture of aldehyde (1 pt.) and water (3 pts.) boils at 37°. Aldehyde dissolves S, P, and I. Burns with blue flame. It dissolves 7 times as much SO_2 as water does.

Tests.—1. Heated with ammoniacal silver nitrate forms a mirror.—2. Heated with aqueous potash forms a yellow body (aldehyde resin) and gives off a characteristic odour (Weidenbusch, *A.* 66, 153). The solution then contains formate and acetate.—3. Restores the colour to a solution of a rosaniline salt that has been bleached by SO_2.—4. Reacts with hydroxylamine forming a liquid oxim (*v. infra*).—5. Reacts with phenylhydrazine forming a crystalline phenyl-hydrazide (*v. infra*).—6. Combines with $NaHSO_3$.—7. Combines with NH_3.—8. H_2S passed into an aqueous solution forms an oil, converted by acids into solid thio-aldehyde (*q. v.*).—9. Alkaline aqueous solutions produce a red coloration when treated with diazo-benzene sulphonic acid and a little sodium-amalgam.

Reactions.—1. *Oxidised* to acetic acid slowly by *air*, more rapidly in presence of platinum black, most rapidly by oxidising agents.—2. Passed over red-hot *soda lime*, it forms sodic acetate and hydrogen. Passed over red-hot *quicklime*, it gives acetone and various ketones and gases (Schloemilch, *Z.* [2] 5, 336).—3. HI at high temperatures reduces it to ethane (Berthelot, *Bl.* [2] 7, 59).—4. *Sodium amalgam* reduces it to alcohol, some di-oxy-butane being also formed (Kekulé, *A.* 162, 309).—5. Converted into crotonic aldehyde (*q. v.*) by $ZnCl_2$ or by aqueous solutions of *sodic acetate* or *Rochelle salt* at 100°. *Zinc shavings* at 100° produce an aldehyde $C_8H_{14}O_2$ (220°); it is an oil and combines with $NaHSO_3$ (Riban, *Bl.* [2] 18, 63).—6. With *chlorine* forms, in sunlight, acetyl chloride (Wurtz, *A.* 102, 93).—7. *Chlorine* passed into aqueous aldehyde forms chloral, butyro-chloral, dichloraldehyde, and other bodies (Pinner, *A.* 179, 21; *B.* 8, 1321, 1561; Wurtz a. Vogt, *Bl.* 17, 402). *Bromine* converts aldehyde, dissolved in acetic ether, into bromal and di-bromo-aldehyde.—8. PCl_5 gives ethylidene chloride, $CH_3.CHCl_2$ (Beilstein, *A.* 113, 110). $COCl_2$ acts similarly (Eckenroth, *B.* 18, 518).—9. PCl_3Br_2 gives ethylidene bromide, $CH_3.CHBr_2$ (Paterno a. Pisati, *B.* 5, 289).—10. Dry HCl

passed into cold aldehyde forms ethylidene chlorhydrin $CH_3.CHCl.OH$, (25°) at 40 mm. This changes spontaneously, or more quickly if heated or treated with HCl, into 'ethylidene oxy-chloride,' $C_4H_8Cl_2O$, (c. 59°) at 40 mm. A small quantity of another body, $C_8H_{12}Cl_2O$, (c. 100°) at 40 mm., is also got. Ethylidene oxy-chloride is probably di-chloro-di-ethyl oxide $(CH_3.CHCl)_2O$. It is converted by boiling water into aldehyde and HCl, and by ammonia into efflorescent needles of $(CH_3.CHNH_2)_2O\,2HCl$ (Lieben, *C. R.* 46, 662; Kessel, *A.* 175, 46; Hanriot, *C. R.* 92, 302). Aldehyde saturated with HCl is converted into crotonic aldehyde (*q. v.*), chloro-butyric aldehyde, and a compound $C_{10}H_{18}Cl_2O_3$ [98°] (Kekulé, *A.* 162, 102).—11. Aldehyde left for some days with aqueous HCl forms aldol (*q. v.*).—12. HCl passed into a mixture of aldehyde and alcohol forms chloro-ethyl ether (*q. v.*).—13. HCl passed into a mixture of aldehyde and *mercaptan* forms di-thio-acetal $CH_3.CH(SEt)_2$, a mobile liquid (Baumann, *B.* 18, 884).—14. Aldehyde forms with *zinc ethyl* a compound which is decomposed by water with production of secondary butyl alcohol (*q. v.*).—15. When paraldehyde (1 g.) is added to cold H_2SO_4 (100 g.) and the solution is shaken with *benzene*, di-phenyl-ethane is got:

$$CH_3.CHO + 2C_6H_6 = CH_3.CH(C_6H_5)_2 + H_2O$$

(Baeyer, *B.* 7, 1190).—16. With *cyanamide* it forms a compound $(C_2H_4)_3N_3Cy_3Aq$ (Knop, *A.* 131, 253).—17. With HCN it gives lacto-nitrile (*q. v.*). 18. With HCN, HCl, and NH_3 in aqueous solution it gives, on boiling, alanine (*q. v.*). A mixture of aldehyde-ammonia and HCN in 30 p.c. solution acidified by HCl gives in the cold amido-propionitrile, which changes first to imido-propionitrile, and then, in about a month, to hydrocyanaldine.

Hydrocyanaldine $C_9H_{12}N_4$. [115°]. S. ·18 at 20°. S. (alcohol) 1·27 at 18°. Prisms (from ether). May be sublimed. V. sol. acetone, m. sol. ether, v. sl. sol. CS_2. Decomposed into its components by boiling $AgNO_3$ or boiling KOH.

Parahydrocyanaldine $C_9H_{12}N_4$. [232°]. S. ·01 at 20°; S. (alcohol) ·01 at 18°. This is a similar body formed by allowing the liquid containing hydrocyanaldine to stand several months, and also by warming a mixture of amido- and imido- propionitrile with HCl. Rhombic crystals (from acetone). Insol. ether, v. c. sol. acetone. Decomposed by $AgNO_3$ or KOH like hydrocyanaldine.

Combinations.—1. With *bisulphites of the alkalis*: $C_2H_4ONaHSO_3Aq$: pearly plates by evaporation over H_2SO_4; satiny needles when ppd. by alcohol.—$C_2H_4OKHSO_3$: hard indistinct crystals composed of minute needles.—$(C_2H_4O)_2Ba(HSO_3)_2$: soluble scales.—If a solution of $(NH_4)HSO_3$ be mixed with aldehyde and evaporated, it deposits crystals of $C_2H_4OSO_2NH_3$, S. 16 at 16° (Bunte, *A.* 170, 305). But by passing SO_2 into alcoholic aldehyde-ammonia, Redtenbacher (*A.* 65, 37) got unstable needles of an isomeric body, S. 70 at 16°. When strongly heated with potash-lime, this decomposed with production of di-methyl-amine or ethylamine (Gössmann, *A.* 91, 122).—It may be $C_2H_4ONH_4HSO_3$ (Beilstein).—The compound of aldehyde with acid sodium sulphite may perhaps be represented by the formula $CH_3.CH(OH).SO_3Na$, as *a*-oxy-ethyl sodium sulphite.

2. With *ammonia*: $CH_3.CH(OH).NH_2$.

Aldehyde-ammonia [70°–80°]. (100°). V.D. 30·36. By passing NH_3 into ethereal solution of aldehyde (Liebig, *A.* 14, 133). Rhombohedra, best got by mixing a conc. alcoholic solution with ether, very soluble in water, hardly soluble in ether. Alkaline. Turns brown in air. Decomposed by dilute acids, even by CO_2, giving off aldehyde. Reactions.—(*a*) H_2S forms thialdine (*q. v.*).—(*b*) H_2Se forms selen-aldine $C_6H_{13}NSe_2$.—(*c*) Alcoholic CS_2 forms carbo-thialdine (*q. v.*).—(*d*) HCN and HCl form, in the cold, hydrocyanaldine, $C_9H_{12}N_4$, or on heating, alanine (*q. v.*).—(*e*) At 120° in a sealed tube it forms tri-methyl-pyridine, *oxy-tetraldine* $C_8H_{13}NO$, and *oxypentaldine* $C_{10}H_{15}NO$. The two latter are monacid amorphous bases, sl. sol. water (Babo, *J. pr.* 72, 88; Heintz a. Wislicenus, *J.* 1858, 347; Schiff, *A. Suppl.* 6, 10).—(*f*) Action of SO_2 is described above.—(*g*) CS_2 forms carbothialdine $C_5H_{10}N_2S_2$ (*q. v.*).—(*h*) NaOEt and MeI in the cold form isocholine iodide, $C_5H_{14}NOI$ (G. Meyer, *B.* 16, 207).

3. With *ammonia* and *silver nitrate* or *sulphate*: When $AgNO_3$ (100 c.c. of a $\frac{3}{5}$ normal solution) is added to aqueous NH_3 (15 c.c. four times normal) and, after filtration, aldehyde is added as long as the pp. first formed redissolves, a liquid is got in which more NH_3 (15 c.c.) causes separation of the compound $C_4H_{10}N_3O_3Ag\,\frac{1}{2}aq$, which must be washed with alcohol and ether and dried at a low temperature (Reychler, *B.* 17, 41). It forms unstable white six-sided plates. Sl. sol. water, v. sl. sol. alcohol, insol. ether. Its warm aqueous solution deposits a silver mirror.—If the same solutions be mixed in the following proportions: 20 c.c. NH_3Aq, 33 c.c. $AgNO_3Aq$ and 20 c.c. aldehyde, and 250 c.c. alcohol be added, a white microcrystalline pp. $C_4H_{10}N_3O_3Ag$ is got. This body is represented by Liebermann a. Goldschmidt (*B.* 10, 2179; 11, 1198) as $AgNO_3 2C_2H_4NH$;

Reychler writes $AgO.N\,(<^{NH}_{O}>CH.CH_3)_2$.—$Ag_2SO_4(C_2H_4NH)_4 3aq$.—$Ag_2SO_4(C_2H_4NH)_4 6aq$.—$Ag_2SO_4(C_2H_4NH)_3NH_3\,3aq$ (W. G. Mixter, *Am. S.* [3] 17, 427).

4. A solution of aldehyde in *alcoholic ammonia* in six months becomes brown. If it be then evaporated, *tri-ethylidene diamine*, or *hydracetamide* $(CH_3.CH)_3N_2$, is left as a yellow amorphous powder, soluble in water. Its hydrochloride is $C_6H_{12}N_2 2HCl$. Boiling water or acids convert it into *oxy-trialdine* $C_6H_{11}NO$, an amorphous yellow powder, soluble in water; salts.—$C_6H_{11}NO.HCl$.—$(C_6H_{11}NO)_2H_2SO_4$ (H. Schiff, *Bl.* [2] 8, 443; *A. Suppl.* 6, 1).

5. With *prussic acid*: C_2H_4OCNH *i. e.* $C_2H_4(OH)CN$, *ethylidene cyanhydrin* or lacto-nitrile (*q. v.*).—6. With *ethyl nitrate*: $C_2H_4O2EtNO_3$ (86°). S.G. $\frac{12}{}$ 1·045. Formed by distilling a mixture of $KEtSO_4$ with KNO_3. It is an oil. Vapour explosive. Decomposed by potash into aldehyde (Nadler, *A.* 116, 173).

7. With *ethyl chloride v.* CHLORO-DI-ETHYL OXIDE.

8. With *alkoyl chlorides* or *bromides*. The following compounds may be viewed as derived from ethylidene glycol chlorhydrin $CH_3.CH(OH)Cl$ (*v.* reaction 10), by displacement of H by acid radicles.

(*a*) **With** ***acetyl chloride*: C_2H_4O, $C_2H_3O.Cl$ or $C_2H_4(OAc)Cl$, *ethylidene chloracetin*** (121·5° cor.) S.G. $\frac{15}{}$ 1·114. Combination takes place at 100° (M. Simpson, *Pr.* 27, 120; Franchimont, *R.* 1, 246; Rübencamp, *A.* 225, 274). The compound was discovered by Wurtz (*Z.* 1871, 362; *A. Ch.* [3], 49, 58; *C. R.* 73, 528). Decomposed by potash into KCl, acetic acid, and aldehyde. KOAc forms $CH_3.CH(OAc)_2$ (Schiff, *B.* 9, 304). Chlorine at 120°, in presence of iodine, forms $CHCl_2.CHCl.OAc$, tri-chloro-ethyl acetate (250°–280°). Bromine dropped into it at 100° forms bromethyl bromo-acetate $CH_3.CHBr.O.CO.CH_2Br$ (*v.* BROMO-ACETIC ACID).

(*b*) With *acetyl bromide* forms a corresponding, but unstable, compound (c. 140°) (Tawildaroff, *A.* 176, 21).

(*c*) With *propionyl chloride*: $C_5H_9ClO_2$ or $CH_3.CHCl.O(C_3H_5O)$, *chloro-ethyl-propionate* (135° uncor.). S.G. $\frac{15}{}$ 1·071.

(*d*) With *butyryl chloride*: $CH_3.CHCl.O(C_4H_7O)$ (149° uncor.). S.G. $\frac{15}{}$ 1·038.

(*e*) With *valeryl chloride*: $CH_3.CHCl.O(C_5H_9O)$ (c. 163°). S.G. $\frac{15}{}$ ·997.

DERIVATIVES OF ORTHO-ALDEHYDE.

The following combinations between aldehyde and compounds of the form M_2O may be viewed as derivatives of ortho-aldehyde, $CH_3.CH(OH)_2$. Ortho-aldehyde itself is not known, but chloral hydrate is tri-chloro-ortho-aldehyde.

Alkyl derivatives, Acetals or *Aldehydates.* The term 'acetal,' originally applied to $CH_3.CH(OEt)_2$, is now often extended to the whole series of di-alkylated ortho-aldehydes.

These bodies are formed, together with other products, by the oxidation of alcohols. Each of them may be formed from one of its higher homologues, by heating the latter at 120°, with an alcohol containing a lower radicle. Thus di-ethyl-acetal heated with methyl alcohol yields dimethylacetal, whereas the latter heated with ethyl, propyl, isobutyl, or amyl alcohol yields only traces of an acetal containing different alcohol-radicles. Similarly diethyl-acetal heated with methyl-alcohol is converted, for the most part, into dimethylacetal, but is practically unaltered by propyl and amyl alcohols (Bachmann, *A.* 218, 38). Aldehydates may also be formed by heating aldehydes with alcohols and HCl (Wurtz a. Frapolli, *A.* 108, 226; Claus a. Trainer, *B.* 19, 3004).

Ethyl-ortho-aldehyde $CH_3.CH(OH)(OEt)$ (80°–90°) (Rénard, *B.* 8, 132) (c. 50°) (Jacobsen, *B.* 4, 215). Among the products of electrolysis of mixture of alcohol and dilute H_2SO_4 (R.). By action of water on chloro-ethyl-ether, $CH_3.CHCl.OEt$ (J.).

Di-methyl-acetal $C_4H_{10}O_2$ *i.e.* $CH_3.CH(OMe)_2$ (62·7°–63·3°) at 751·6 mm. S.G. $\frac{22}{}$ ·8655 (Bachmann); ·8590 at 14° (Dancer, *A.* 132, 240). V.D. 3·10 (for 3·11). S.V. 110·81 (R. Schiff, *A.* 220, 104). Occurs in crude wood spirit (D.). Formed by oxidising a mixture of MeOH and EtOH with MnO_2 and H_2SO_4 (Wurtz). Prepared by heating aldehyde (4 vols.), methyl alcohol (8 vols.), and glacial HOAc (1 vol.) at 100° (Alsberg, *J.* 1864, 485). A colourless liquid burning with a white, blue-edged flame (Wurtz, *A. Ch.* [3] 48, 373). EtOH at 120° has hardly any action, traces of methyl-ethyl-acetal being formed. Propyl, isobutyl, and iso-amyl alcohols act similarly.

Methyl-ethyl-acetal $CH_3.CH(OMe)(OEt)$. Reactions that might be expected to produce this body yield only a mixture of di-methyl-acetal and di-ethyl-acetal (A. Geuther, *A.* 226, 265).

Di-ethyl acetal v. ACETAL.

Methyl-propyl-acetal $C_6H_{14}O_2$ *i. e.* $CH_3CH(OMe)(OPr)$ (103°–105°). Very little is formed from di-methyl-acetal and PrOH at 120°.

Ethyl-propyl-acetal $C_7H_{16}O_2$ *i. e.* $CH_3.CH(OEt)(OPr)$ (124°–126°). Very little is formed from di-ethyl-acetal and PrOH at 120°.

Methyl-isobutyl-acetal $C_7H_{16}O_2$ (126°). Dimethyl-acetal (15 g.) heated with isobutyl alcohol at 120° forms a little (1 g.) of this body.

Methyl-iso-amyl-acetal $C_8H_{18}O_2$ (141°–144°). A little got from di-methyl-acetal and iso-amyl alcohol at 120°.

Di-propyl-acetal $C_8H_{18}O_2$ (146°–148°). S.G. $\frac{22.5}{}$ ·825. Got by passing pure PH_3 into a mixture of aldehyde and PrOH at −21° (Girard, *C. R.* 91, 629).

Di-iso-butyl-acetal $C_{10}H_{22}O_2$ (168°–170°). S.G. $\frac{22}{}$ ·816. Prepared like the preceding.

Di-iso-amyl-acetal $C_{12}H_{26}O_2$ *i. e.* $CH_3.CH(OC_5H_{11})_2$ (c. 195°) (Bachmann); (210·8° cor.) (Alsberg, *J.* 1864, 485; Claus a. Trainer, *B.* 19, 3008). S.G. $\frac{22}{}$ ·801 (B.); $\frac{15}{}$ ·835 (A.). Aldehyde (1 vol.) and iso-amyl alcohol (5 vols.) are mixed, saturated with SO_2 and warmed with glacial HOAc (1 vol.). A small quantity is got by heating amyl alcohol with acetal at 120°.

Ethylene-acetal $C_4H_8O_2$ *i. e.*

$CH_3CH{<}^{O}_{O}{>}C_2H_4$ (82·5°) at 766 mm. S.G. $\frac{0}{}$ 1·002. S. 67. From aldehyde and glycol at 100° (Wurtz, *A.* 120, 328). Separated by $CaCl_2$ from its aqueous solution. Not attacked by KOH. Acetic acid gives glycol di-acetin.

Propylene-acetal $C_5H_{10}O_2$ *i. e.*

$CH_3.CH{<}^{O}_{O}{>}C_3H_6$ (93°). From aldehyde and propylene glycol at 160° (Gramont, *Bl.* 41, 361). Decomposed by water into aldehyde and propylene glycol.

Oxy-propylene-acetal $C_5H_{10}O_3$

i.e. $CH_3.CH{<}^{O}_{O}{>}C_3H_5OH$ (c. 186°) S.G. $\frac{0}{}$ 1·081.

From aldehyde and glycerin at 180° (Harnitzky a. Menschutkin, *A.* 136, 126). Decomposed by water into its components.

Di-(β)-naphthyl-acetal $C_{22}H_{18}O_2$ *i.e.* $CH_3.CH(O.C_{10}H_7)_2$. [201°]. Slowly formed when (β)-naphthol and aldehyde are dissolved in acetic acid and a few drops of HCl are added (Claisen, *B.* 19, 3318). Crystals; insol. aqueous alkalis. Changed by warming with HOAc and HCl into ethylidene-di-naphthyl oxide,

$$CH_3.CH{<}^{C_{10}H_6}_{C_{10}H_6}{>}O.$$

Alkoyl derivatives or *ethylidene salts.* When both alkoyls (acid radicles) are the same, these bodies may be viewed as compounds of acid anhydrides with aldehyde. They are slowly decomposed by water, more rapidly by potash, into aldehyde and acids. Mono-alkoyl derivatives, $CH_3.CH(OH)(OR)$ are not known; they appear to split up into water and the an-

hydrides $\{CH_3.CH(OR)\}_2O$. These anhydrides may be formed from di-chloro-di-ethyl oxide, $(CH_3CHCl)_2O$ and sodium salts. They are volatile liquids, decomposed by water into aldehyde and acid (Geuther, *A.* 226, 223).

Di-acetyl derivative $CH_3.CH(OAc)_2$ (168·4° cor.). S.G. $\frac{15}{}$ 1·073. μ = 1·40 at 28°. 1. From $CH_3.CHCl(OAc)$ and AgOAc (Rübencamp, *A.* 225, 274).—2. From aldehyde and Ac_2O at 180° (Geuther, *A.* 106, 249).—3. From aldehyde and AcCl at 100° (Franchimont, *R.* 1, 248).

Di-propionyl derivative $CH_3.CH(OC_3H_5O)_2$ (192·2° cor.). S.G. $\frac{15}{}$ 1·020 μ = 1·407. From $CH_3.CHCl(OC_3H_5O)$ and $AgO(C_3H_5O)$.

Di-butyryl derivative $CH_3.CH(OC_4H_7O)_2$ (215·5° cor.). S.G. $\frac{15}{}$ ·9855. μ = 1·411.

Di-valeryl derivative $CH_3.CH(OC_5H_9O)_2$ (225° cor.). S.G. $\frac{15}{}$ ·947. μ = 1·414.

Acetyl-propionyl derivative $CH_3.CH(OAc)(OC_3H_5O)$ (178·6° cor.). S.G. $\frac{15}{}$ 1·044 μ = 1·402. From $AgOC_3H_5O$ and $CH_3.CHCl.OAc$ or from AgOAc and $CH_3.CHCl.OC_3H_5O$ (Geuther a. Rübencamp, *A.* 225, 281).

Acetyl-butyryl derivative $CH_3.CH(OAc)(OC_4H_7O)$ (192·6° cor.). S.G. $\frac{15}{}$ 1·015 μ = 1·047. From $AgOC_4H_7O$ and $CH_3.CHCl.OAc$, or from AgOAc and $CH_3.CHCl.OC_4H_7O$.

Acetyl-valeryl derivative $CH_3.CH(OAc)(OC_5H_9O)$ (194°–199° cor.). S.G. $\frac{15}{}$ ·991 μ = 1·408. Similarly prepared.

POLYMERIDES OF ALDEHYDE.

Aldehyde readily polymerises, forming aldol $C_4H_8O_2$ (*q. v.*), paraldehyde $C_6H_{12}O_3$, or metaldehyde $C_{2n}H_{4n}O_n$. Pure aldehyde may be kept without change, but when impure it spontaneously changes to paraldehyde or metaldehyde (Weidenbusch, *A.* 66, 155; Fehling, *A.* 27, 319; Geuther a. Cartmell, *A.* 112, 16; Lieben, *A. Suppl.* 1, 114; Kekulé a. Zincke, *A.* 142, 141; *B.* 3, 468). Metaldehyde is formed from aldehyde at a low temperature by the same reagents that cause the formation of paraldehyde at high temperatures (K. a. Z.). Neither of these bodies is affected by hot potash, but both of them are converted by PCl_5 into ethylidene chloride, $CH_3.CHCl_2$, and by HCl into 'ethylidene oxy-chloride' (*v. supra*). A little alcoholic KOH converts aldehyde into a mixture of metaldehyde, paraldehyde, and a little crotonic aldehyde (Perkin, *C. J.* 43, 88).

Paraldehyde $C_6H_{12}O_3$. Mol. w. 132. [10°–12°]. (124° i. V.) (K. a. Z.); (124·4°) at 752mm. (R. Schiff, *A.* 220, 104). S.G. $\frac{20}{}$ ·9943 (Brühl); $\frac{15}{15}$ ·9993; $\frac{}{4}$ ·9900 (Perkin, *C. J.* 45, 479). S.V. 150·7 (S.). V.D. 4·35 (for 4·55, S.). μ_β 1·4095. R_∞ 52·48 (B.) M.M. 6·662 at 17°. S. 12 at 13°; 6 at 100°.

Preparation.—In presence of a small quantity of HCl, $COCl_2$, or SO_2, aldehyde gradually becomes hot, often reaching 40°. It is then changed to paraldehyde. H_2SO_4 and $ZnCl_2$ effect this change even more vigorously. The product is cooled to 0°, when paraldehyde crystallises.

Properties.—Colourless liquid, smelling like acetal and aldehyde. It is partially converted into aldehyde by distillation. Distillation with H_2SO_4, HCl, $ZnCl_2$, $HgBr_2$, or $COCl_2$ completely effects this change. The reactions of paraldehyde, in presence of any of these bodies, are therefore the same as those of aldehyde. It also forms $CH_3.CH(OAc)_2$ with Ac_2O. But it does not react with ammonia. HNO_3 oxidises it to glyoxal (Liubawin, *J. R.* 13, 496).

Constitution. — The S.V. agrees with that required by Kekulé's formula

$$C_2H_4\!<\!\begin{smallmatrix}O.C_2H_4\\O.C_2H_4\end{smallmatrix}\!>\!O$$ (Brühl, *A.* 203, 44).

Metaldehyde $C_6H_{12}O_3$. S. (chloroform) 1·034 at 26°; 4·235 at 60°; S. (benzene) ·12 at 23°, ·181 at 80°. Formed by passing a few bubbles of SO_2 or HCl into aldehyde in a freezing mixture; metaldehyde crystallises out, and the mother liquors are distilled and treated as before (K. a. Z.). $CaCl_2$ effects the same transformation at the ordinary temperature.

Properties.—Long striated prisms, sublimes about 115° without melting. Insoluble in water, slightly soluble in cold alcohol or ether. It may be converted into aldehyde: (a) by heating for a day *in vacuo* at 180°, (b) by repeatedly distilling under atmospheric pressure, (c) by heating its solution in chloroform. The vapour density may be found in the usual way, due allowance being made for its partial dissociation, the amount of undecomposed metaldehyde being estimated after cooling. The V.D. is thus found to lie between 72·2 and 59·1, the mean value being 62·5. Metaldehyde is not attacked in the cold by $KMnO_4$, chromic mixture, or NH_3. *Chlorine* forms chloral; PCl_5 gives ethylidene chloride (Hanriot a. Oeconomides, *C. R.* 93, 463; *A. Ch.* [5] 25, 226).

Di-aldehyde *v.* ALDOL.

ALDEHYDE-ACETAMIDE $C_6H_{12}N_2O_2$ *i.e.* $CH_3.CH(NHAc)_2$ *di-acetyl-ethylidene diamine* [169°]. Got by heating aldehyde with acetamide (Tawildaroff, *B.* 5, 477).

ALDEHYDE ACETATE *v.* p. 106, *l.* 6.

ALDEHYDE ACETYL CHLORIDE *v.* p. 105, *l.* 1.

ALDEHYDE ALCOHOLATE *v.* p. 105, *l.* 53.

ALDEHYDE GREEN *v.* ROSANILINE.

ALDEHYDE GUM $C_{10}H_{18}O_4$. The barium salt is formed by allowing a solution of aldehyde in baryta-water to stand for some time. From this salt H_2SO_4 liberates the 'gum' as a syrup, soluble in water and alcohol. It reddens rosaniline decolorised by SO_2, and it gives iodoform with I and Na_2CO_3. Reduces hot Fehling's solution—$Ca(C_{10}H_{17}O_4)_2$: amorphous (Tollens, *B.* 17, 660).

ALDEHYDE PHENYL-HYDRAZIDE $C_8H_{10}N_2$ *i.e.* $CH_3.CH:N_2HPh$. From aldehyde and phenyl-hydrazine in ether *v.* ALDEHYDES, *reaction* 4. Crystallised from benzoline. Deliquescent. V. sol. alcohol or ether. Resolved by boiling water or dilute acids into its constituents.

ALDEHYDE RESIN. Formed by the action of aqueous or alcoholic potash, hot or cold, upon aldehyde, or by heating aldehyde with NaOAc in sealed tubes at 100°. It is accompanied by a strongly smelling yellow oil which may be removed by distillation. Aldehyde resin resembles colophony. It produces, when fused with potash, oxy-iso-phthalic acid [283°], *o*-oxy-*m*-toluic acid [173°], and *m*-xylenol, $C_6H_3Me_2OH$ When strongly heated with zinc dust it gives ethyl-benzene, *m*- and *p*- methyl-ethyl-benzene and methyl-naphthalene. Conc. HNO_3 gives

iso-phthalic acid (Weidenbusch, *A.* 66, 153; Ciamician, *M.* 1, 199).

ALDEHYDES.—An aldehyde is a body derived from a primary alcohol by removal of two atoms of hydrogen from each molecule, and having the general formula R.CO.H. It may therefore be looked upon as a ketone in which one alkyl is represented by H. Aldehydes may also be viewed as hydrides of acid radicles, hence CH_3.CO.H is called *acetic* aldehyde and not *ethyl* aldehyde, although the latter name is, etymologically, the more correct (p. 103).

Enumeration.—In the following list the numbers denote values of *n*. $C_nH_{2n}O$. 1. Formic; 2. Acetic; 3. Propionic; 4. Butyric; 5. Valeric; 6. Hexoic; 7. Heptoic; 10. Decoic; 12. Lauric; 14. Myristic; 16. Palmitic; 17. Stearic.—$C_nH_{2n-2}O$. 3. Acrylic (acroleïn); 4. Crotonic; 5. Tiglic; 6. Hexenoic; 8. Octenoic; 14. Tetradecenoic; 15. Cimicic; 21. Tri-œnanthic.— $C_nH_{2n-6}O$. $C_{21}H_{30}O$, Tetra-œnanthic. — $C_nH_{2n-8}O$. Benzoic; Phenyl-propionic. — $C_nH_{2n-10}O_2$. Cinnamic.—$C_nH_{2n-14}O$. Naphthoic. —$C_nH_{2n-16}O$. Di-phenyl-acetic.—$C_nH_{2n}O_2$. Glycollic (?). Oxypropionic. Oxybutyric (aldol). — $C_nH_{2n-2}O_2$. Glyoxal. — $C_nH_{2n-4}O_2$. Maleic. — $C_nH_{2n-6}O_2$. Furfurol.—$C_nH_{2n-8}O_2$. Oxy-benzoic; Furfur-acrylic, Furfurcrotonic. — $C_nH_{2n-2}O_3$. Suberic. Azelaïc and Brassylic.—$C_nH_{2n-4}O_3$. Di-oxy-benzoic; Piperonal. —$C_nH_{2n-10}O_4$ Di-aldehydo-resorcin; Di-aldehydo-orcin.

Formation.—1. By oxidation of primary alcohols by air and platinum-black, by aqueous chromic acid or by H_2SO_4 and MnO_2:

$$2R.CH_2.OH + O_2 = 2R.CO.H + 2H_2O.$$

2. By distilling a mixture of barium or calcium formate with some barium or calcium salt: $Ca(O.CO.R)_2 + Ca(O.CO.H)_2 = 2CaCO_3 + 2H.CO.R$ (Limpricht, *A.* 97, 368; Piria, *A. Ch.* [3] 48, 113; Krafft, *B.* 16, 1717). This process is a particular case of Williamson's method of producing mixed ketones. Instead of calcic formate, a mixture of calcic oxalate and lime may be used (Bogusch, *J. R.* 7, 47).—3. From chlorides of the type $R.CH.Cl_2$ by heating with dry oxalic acid (Anschütz, *A.* 226, 19).—4. Chromyl dichloride, CrO_2Cl_2, unites with toluene and its homologues when added to their solution in CS_2, forming brown powders, possibly of the form $RCH(O.CrCl_2.OH)_2$, which are decomposed by water with production of aldehydes (A. Etard, *C. R.* 90, 534; 97, 909; Bornemann, *B.* 17, 1462).—5. Aromatic aldehydes may be prepared by heating dichlorides $R.CHCl_2$ with NaOHAq, or the monochlorides, $R.CH_2Cl$ with aqueous lead or copper nitrate.—6. Alcohols of the form R.CH:CH.OH appear to change, at the moment of their formation into aldehydes, $R.CH_2.CHO$. The formation of acroleïn from glycerin, and of aldehyde from bromo-ethylene are instances.—7. Some aldehydes, as benzoic, acetic, propionic, and butyric, are produced by distilling albumen, fibrin, caseïn, or gelatin, with MnO_2 and H_2SO_4. 8. Many aldehydes can be obtained from essential oils derived from plants; *e.g.*, benzoic, cinnamic, cuminic, and salicylic aldehydes.

Properties.—Almost all are volatile liquids.

Reactions.—1. Are readily *oxidised* to acids, and consequently are powerful reducing agents. Ketonic alcohols, $R.CO.CH_2OH$, resemble aldehydes in reducing power (Zincke, *A.* 216, 317).—2. Many are converted by alcoholic *potash* or by potash-fusion into an alcohol and an acid:

$$2C_6H_5.CHO + KOH = C_6H_5.CO_2K + C_6H_5.CH_2OH.$$

Glycols with double the number of carbon atoms in the molecule are often formed.—3. *Sodium-amalgam*, or zinc and glacial HOAc, reduce them to alcohols (Krafft, *B.* 16, 1714; Tiemann, *B.* 19, 355).—4. They combine with $NaHSO_3$. These compounds are usually soluble in water and in alcohol, but insoluble in saturated solutions of the bisulphites. Hence by shaking a liquid containing an aldehyde with excess of such a saturated solution, the aldehyde may be completely separated in the form of a crystalline compound. From these compounds the aldehyde may be set free by dilute H_2SO_4 or Na_2CO_3, and may then be distilled with steam (Bertagnini, *A.* 85, 179, 268).—5. They combine with *phenylhydrazine* (*q. v.*). A solution of phenyl-hydrazine hydrochloride (1 pt.) and sodic acetate ($1\frac{1}{2}$ pts.) in water (8 pts.) when added to an aqueous solution of an aldehyde or ketone, produces an insoluble compound, usually an oil appearing in drops producing a milkiness, but sometimes a crystalline pp. These compounds are not volatile with steam, but on boiling with dilute HCl they are resolved into phenyl-hydrazine hydrochloride and the aldehyde or ketone (E. Fischer, *A.* 190, 131; *B.* 15, 2252).—6. They form a silver mirror when heated with conc. ammoniacal *silver nitrate*. The reduction is promoted by adding NaOH (Tollens, *B.* 15, 1635). 7. A solution of a *rosaniline* salt, bleached by SO_2, is reddened by aldehydes, in the cold (Schiff, *Z.* 1867, 175; Caro; V. Meyer, *B.* 13, 2342). This test is not infallible (Tiemann, *B.* 14, 791); it is given by aldehyde, paraldehyde, propionic, iso-valeric, and œnanthic aldehydes, chloral, butyro-chloral, acroleïn, furfurol, benzoic, cinnamic, and furfurcrotonic aldehydes, furfuracroleïn, salicylic aldehyde, cimicic aldehyde; it is not given by chloral hydrate, formic acid, carbo-hydrates, propyl alcohol and higher alcohols, pinacone, glycol, the phenols, or quinone; a faint colour is produced after some time by acetone, and methyl and ethyl alcohols (G. Schmidt, *B.* 14, 1848).—8. Alkaline aqueous solutions produce a coloration like magenta when treated with *diazo-benzene sulphonic acid* and a little sodium-amalgam. Acetone and aceto-acetic ether give a dark red coloration without the violet shade (Penzoldt a. E. Fischer, *B.* 16, 657).—9. Aldehydes are converted by *hydroxylamine* into aldoxims:

$$R.CHO + H_2NOH = R.CH:NOH + H_2O$$

(V. Meyer, *B.* 15, 1164, 1324, 1525, 2784; 16, 822, 2992).—10. *u-di-methyl-p-phenylene diamine* acts vigorously on aldehydes in alcoholic solution forming crystalline compounds (A. Calm, *B.* 17, 2938): $Ph.CHO + NH_2.C_6H_4.NMe_2 = Ph.CH:N.C_6H_4.NMe_2 + H_2O$.

11. Homologues of acetic aldehyde form crystalline compounds with *ammonia*, $R.CH(NH_2)OH$. These are converted by H_2S into sulphur bases (*v.* p. 104, *l.* 9). The aromatic aldehydes are converted by ammonia into hydramides:

$$3Ph.CHO + 2NH_3 = (Ph.CH)_3N_2 + 3H_2O.$$

Some fatty aldehydes, *e.g.* iso-butyric aldehyde (Lipp, *A.* 211, 344) behave similarly. Acroleïn loses only half its oxygen:

$$2C_3H_4O + NH_3 = C_6H_9NO + H_2O.$$

Primary and secondary bases act upon aldehydes with elimination of water. The neutral products are split up by HCl into their components. 12. *Chlorine* forms derivatives by substitution.—**13.** PCl_5 displaces O by Cl_2.—**14.** H_2S displaces O by S, forming thio-aldehydes, or their polymerides.—15. PCl_3 combines with aldehydes; the compounds are converted by water into phosphinic acids (*q.v.*).—16. PH_4I forms crystalline compounds (*v.* PHOSPHINES).—17. Aldehydes react with *alcohols* forming acetals (p.):

$$R.CHO + 2HOR' = R.CH(OR')_2 + H_2O.$$

Similarly, *mercaptans* form mercaptals (Baumann, *B.* 18, 884).—18. *Alkyl chlorides* form chlorinated ethers (*e.g.* $CH_3CHCl.OEt$). Alkoyl chlorides act similarly (p. 105, *l.* 1).—19. *Hydric cyanide* combines with aldehydes, forming α-oxy-nitriles. These nitriles give (*a*) on saponification, oxy acids, (*b*) on treatment with ammonia, amido-nitriles, whence amido acids may be got (Tiemann, *B.* 14, 1965).—20. Aldehydes may be converted into amido-acids by allowing them to stand for 30 minutes with a 3 p.c. solution of NH_4CN, and then boiling with HCl (Liubawin, *J. R.* 13, 506).—21. Benzoic aldehyde reacts with *nitro-paraffins* thus: $Ph.CHO + H_2C(NO_2).CH_3 = Ph.CH{:}C(NO_2).CH_3 + H_2O$ (Priebs, *A.* 225, 319). 22. Aldehydes condense with *aromatic compounds* with elimination of H_2O and formation of tri-substituted methanes. Thus aldehyde and benzene give di-phenyl-methyl-methane; benzoic aldehyde and phenol give di-oxy-tri-phenyl-methane; benzoic aldehyde and aniline give di-amido-tri-phenyl-methane.—23. In presence of small quantities of acids, aldehydes form red resins when warmed with *phenols*. Many of these are converted by excess of acids into crystalline isomerides. Thus benzoic aldehyde forms with pyrogallic acid prisms (from ether) of $C_{26}H_{20}O_6$; this forms an acetyl derivative $C_{26}H_{24}Ac_2O_6$. Benzoic aldehyde and resorcin form $C_{26}H_{20}O_4$. If a few drops of a liquid containing an aldehyde be boiled with an alcoholic solution of resorcin and a little HCl, and be then poured into water, a pp. is formed. This may be used as a test for presence of aldehydes (Baeyer, *B.* 5, 25; Michael a. Ryder, *B.* 19, 1388).—24. In dilute *alkaline solution* aldehydes condense with *ketones* or *other aldehydes* with elimination of H_2O, and production of complicated aldehydes or ketones.—25. For the reaction between aldehydes and *o-di-amines v.* ALDEHYDINES.

PERKIN'S SYNTHESIS OF UNSATURATED ACIDS.—Benzoic aldehyde, acetic anhydride and sodic acetate, heated together form sodic cinnamate.

In this reaction the sodic acetate may be exchanged for sodic butyrate or valerate, but the product will still be sodic cinnamate: hence Perkin concludes that the reaction takes place between the aldehyde and the anhydride. Fittig came to the opposite conclusion, viz., that the aldehyde acted on the sodium salt and that the nature of the anhydride was immaterial, thus if sodic succinate and acetic anhydride were used, the condensation took place with the sodic succinate. To this Tiemann (*B.* 15, 2061) objected that possibly the acetic anhydride acting on the sodic succinate formed sodic acetate and succinic anhydride, and that the latter reacted upon the aldehyde. Stuart (*B.* 16, 1436) then showed that when sodic malonate was used condensation took place between it and the benzoic aldehyde, although no malonic anhydride is known. He also showed that in this case glacial acetic acid might be substituted for acetic anhydride. According to Fittig, aldol-like condensation-products are first formed, and these, when they split off water, give the unsaturated acids (*A.* 227, 49). This is shown by the action of sodic iso-butyrate on benzoic aldehyde in presence of isobutyric anhydride, when the anhydride of the isobutyric derivative of β-oxy-β-phenyl-valeric acid $Ph.CH(OH).CMe_2.CO_2H$ (*q.v.*) is formed; in which there is no H for the OH to split off with. If NaOAc be used instead of sodium isobutyrate oxy-phenyl-valeric acid is still formed, a result that supports Perkin's view (Perkin, *C. J.* 49, 317).

Œnanthol and valeric aldehyde may be substituted for benzoic aldehyde in these syntheses, while the sodium salt and anhydride of propionic or *n*-butyric acid may be used instead of the corresponding derivatives of acetic acid. Condensation then takes place in the α position:

$$Ph.CHO + CH_3.CH_2.CO_2Na = Ph.CH{:}CMe.CO_2Na + H_2O.$$

A dibasic acid can unite with one equivalent of an aldehyde for each $CH_2.CO_2H$ contained in its formula; the product may then lose H_2O, becoming a lactonic acid or an unsaturated acid.

ALDEHYDINES.—This name was formerly applied to the base $C_8H_{11}N$ obtained by heating aldehyde-ammonia, since shown to be tri-methyl-pyridine (*q. v.*). The same name has since been used by Ladenburg (*B.* 10, 1126; 11, 590, 1650) to denote bases obtained by mixing dilute aqueous solutions of aromatic *o* (but not *m* or *p*) di-amine hydrochlorides with aldehydes. Condensation occurs with evolution of heat; the yield of aldehydine after crystallisation is 60 to 70 p.c. of the theoretical. $C_xH_y(NH_2)_2 + 2H.CO.R = C_xH_yN_2C_2H_2R_2 + 2H_2O$. Thus *o*-tolylene-di-amine hydrochloride and benzoic aldehyde give rise to $C_7H_6N_2C_2H_2Ph_2$ tolylene benzaldehydine.

The same body is formed by the action of benzyl chloride on anhydro-benzoyl-tolylene di-amine at 160°, $C_7H_6\left<\begin{matrix}N=C.Ph\\ \diagup \\ NH\end{matrix}\right.$. Hinsberg concludes from this that its formula is

$C_7H_6\left<\begin{matrix}N=C.Ph\\ \diagup \\ N—CH_2Ph\end{matrix}\right.$ (*B.* 19, 2025). Under the conditions of this experiment molecular change is more likely to occur than in the usual preparation of aldehydines in aqueous solution. All other considerations point to a symmetrical formula; and since in stability and other properties these bodies resemble the quinoxalines it is probable that, together with the latter, they belong to the class of azines: tolylene benzaldehydine would then be $C_7H_6\left<\begin{matrix}N-CHPh\\ | \quad\quad | \\ N-CHPh\end{matrix}\right.$. The formula given by Ladenburg is

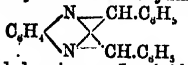
$$C_7H_6\left<\begin{matrix}N—CHPh\\ \diagup\!\diagdown \\ N—CHPh\end{matrix}\right..$$

Phenylene-anis-aldehydine $C_{22}H_{20}N_2O_2$ [129°]. **Needles. Soluble in alcohol. Prepared**

by shaking anisic aldehyde with an aqueous solution of *o*-phenylene-diamine hydrochloride.

B'HCl: needles; difficultly soluble in water.

Phenylene-benzaldehydine $C_{20}H_{16}N_2$ *i.e.*


[133°–134°].

Six-sided prisms. Insoluble in water, easily soluble in alcohol and benzene.

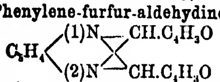
Preparation.—(1) By heating *o*-phenylene-diamine with benzaldehyde. (2) By shaking benzaldehyde with an aqueous solution of *o*-phenylenediamine hydrochloride.

Salts.—B'HCl: colourless prisms. $(B'HCl)_2PtCl_4$: yellow precipitate. $B'HNO_3$. Slightly soluble prisms. $B'_2H_2SO_4$: colourless leaflets.

Ethylo-iodide $C_{20}H_{16}N_2(C_2H_5)I$ [211°–213°]. Colourless prisms.

Methylo-iodide $C_{20}H_{16}N_2(CH_3)I$. Prisms.

Phenylene-furfur-aldehydine $C_{16}H_{12}N_2O_2$ *i.e.*

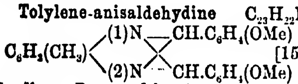

[95°–96°].

Colourless crystals. Soluble in alcohol and C_6H_6, with difficulty in ligroïn, insoluble in water. Prepared by shaking furfurol with an aqueous solution of *o*-phenylenediamine hydrochloride.

Salts. — $(B'HCl)_2PtCl_4$: yellow leaflets. $B'HNO_3$: slightly soluble needles.

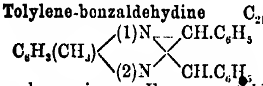
Methylo-iodide $C_{16}H_{12}N_2O_2(CH_3)I$. [192°–195°]. Prisms.

Tolylene-anisaldehydine $C_{23}H_{22}N_2O_2$ *i.e.*


[152°–156°]

Needles. Prepared by the action of anisic aldehyde on an aqueous solution of *o*-tolylene-diamine hydrochloride.

Tolylene-benzaldehydine $C_{21}H_{18}N_2$ *i.e.*


[195·5°].

Colourless prisms. Forms unstable salts with acids. Prepared by heating benzaldehyde with *o*-tolylene diamine to 140°. Yield 45 p.c. of the diamine.

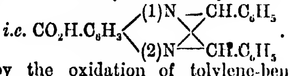
$B'HCl + H_2O$: long needles: difficultly soluble in strong HCl.

Ethylo-iodide [180°–181°]. Needles or prisms ($+\frac{1}{2}H_2O$). Soluble in water. With iodine it forms a periodide $C_{21}H_{18}N_2(C_2H_5)I_3$ [123°].

Gives a strongly alkaline solution with Ag_2O which on neutralising with HCl and adding $PtCl_4$ gives a crystalline platino-chloride $(C_{23}H_{23}N_2Cl)_2PtCl_4$.

Methylo-iodide [209°]. Thin white needles.

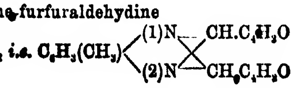
Phenylene-benzaldehydine carboxylic acid

$C_{21}H_{16}N_2O_2$ *i.e.*


Prepared by the oxidation of tolylene-benzaldehydine with $KMnO_4$. Is not altered by heating with HCl to 200°.

Salts: A'Ag: white precipitate. A'_2Ca: difficultly soluble needles.

Tolylene-furfuraldehydine

$C_{17}H_{14}N_2O_2$ *i.e.*


[128½°]. Thin white prisms. Easily soluble in alcohol, ether, &c., with difficulty in cold ligroïn.

Preparation.—(1) By heating furfurol with *o*-tolylenediamine. (2) By adding furfurol (20 pts.) to a solution of *o*-tolylenediamine hydrochloride (20 pts.) in 80 pts. of water; on standing the hydrochloride separates out and is purified by crystallising the base repeatedly from ligroïn; yield 55 p.c. of the theoretical.

Salts: $B'HNO_3$: needles. $B'_2H_2SO_4$: prisms $(B'HCl)_2PtCl_4$: yellow crystals.

Methylo-iodide [195·5°]. Leaflets. Difficultly soluble in water; bitter taste; powerful poison.

Methylo-chloride: leaflets; easily soluble in water. Powerful poison.

Methylo-triiodide $C_{17}H_{14}N_2O_2(CH_3)I_3$ [126°–128°]. Light brown needles.

Methylo-pentiodide $C_{17}H_{14}N_2O_2(CH_3)I_5$ [109°]. Steel-blue pillars.

***p*-ALDEHYDO-BENZOIC ACID** $C_8H_6O_3$ *i.e.* $C_6H_4(CHO)(CO_2H)$ [c. 246°]. Formed by careful oxidation of terephthalic aldehyde with chromic mixture (Löw, *A.* 231, 365; *B.* 18, 947). Needles (from water). Small needles when sublimed. M. sol. ether or chloroform, sl. sol. hot water.

Salt.—AgA'. *Ether.*—EtA'. Shows characters of benzoic aldehyde.

Reactions.—1. Does not reduce ammoniacal $AgNO_3$. Its ethyl ether, however, reduces ammoniacal $AgNO_3$.—2. Does not give Perkin's reaction with NaOAc and Ac_2O.—3. With $ZnCl_2$ and alcoholic $NPhMe_2$ it forms the zinc carboxylate of leuco-malachite green, [147°].

Phenyl hydrazide [226°].

p-*Aldehydo-nitro-benzoic acid*

$C_6H_3\overset{(2)}{(NO_2)}\overset{(1)}{(CHO)}\overset{(4)}{CO_2H}$. *Nitro-terephthalic-aldehyde-acid* [160°]. Large four-sided prisms. Easily soluble in alcohol and ether, sparingly in chloroform. Formed by nitration of *p*-aldehydo-benzoic acid.

With acetone it gives the indigo-reaction (Löw, *B.* 18, 948).

ALDEHYDO-CINNAMIC ACID *v.* CINNAMIC ACID.

ALDEHYDO-NAPHTHOL *v.* OXY-NAPHTHOIC ALDEHYDE.

ALDEHYDO-OXY ACIDS. Got by heating aromatic oxy acids with chloroform and aqueous NaOH (Tiemann a. Reimer, *B.* 9, 1268).

$C_6H_4(ONa)CO_2Na + 3NaOH + CHCl_3 =$
$C_6H_3(COH)(ONa)CO_2Na + 3NaCl + 2H_2O$.

The COH takes either *o* or *p* position towards the hydroxyl.

ALDEHYDO-OXY-BENZOIC ACIDS $C_8H_6O_4$.

m-**Aldehydo-salicylic acid**

$C_6H_3(OH)(CHO)(CO_2H)$[1 : 4 : 2]. [249°]. S. ·7 at 100°; ·038 at 25°.

Preparation.—Salicylic acid (14 pts.), NaOH (25 pts.), water (50 pts.) and chloroform (15 pts.), are boiled for some hours, the product dissolved in water, and acidified with HCl. A yellow pp. is formed and is extracted with ether. The ethereal solution is shaken with aqueous $NaHSO_3$; this solution, when boiled with dilute H_2SO_4, deposits a crystalline pp. consisting of the (1, 2, 6) acid; the (1, 4, 2) acid remaining in the solution, from which it may be extracted by ether (Tiemann a. Reimer, *B.* 9, 1268; 10, 1563).

Properties.—Long delicate yellowish needles. V. sol. ether or hot alcohol, v. sl. sol. chloroform.

action on the skin, affected the colour of many plants, and reacted with acids with effervescence and the production of new substances wherein neither the properties of the acids nor those of the alkalis were prominent. Van Helmont and his successors recognised two kinds of alkali, fixed and volatile; Duhamel, in 1736, divided fixed alkali into two classes, vegetable (potash), and mineral alkali (soda). Little or nothing was known regarding the composition of alkali until the year 1755, when Black (on the occasion of graduating as M.D. at Edinburgh) published his dissertation on 'Magnesia Alba, Quicklime, and other Alkaline Substances.' *Magnesia alba* dissolved in acids with effervescence; but after being strongly heated no effervescence attended the solution of this alkali. The notion of Basil Valentine (end of 15th and beginning of 16th century), that lime when burnt combined with 'matter of fire,' had been accepted by many as an explanation of the difference in the behaviour towards acids of burnt and unburnt lime. If this explanation applied to magnesia it should be possible perhaps to get hold of this 'matter of fire,' which combined with the *magnesia alba* when that body was heated. But Black found that a given mass of *magnesia alba* weighed more than the calcined magnesia obtained from it. Hence something was lost instead of gained during the process of heating. This something proved on further quantitative examination to be a gas different from common air; to it Black gave the name of *fixed air*. The effervescence or non-effervescence of alkalis with acids was proved by Black to accompany the presence or absence of fixed air (carbonic acid). From this time a distinction was clearly drawn between alkalis, which dissolved in acids without effervescence, and carbonated alkalis, the solution of which in acids was accompanied by the escape of carbonic acid gas. It was recognised that whether a caustic or a carbonated alkali were dissolved in an acid, the body which remained in solution, and which had no close resemblance either to the acid or the alkali, was one and the same.

The properties of the alkalis were supposed by the older chemists to be due to a 'principle of alkalinity,' or sometimes to a 'principle of saltness,' which latter principle was common to acids, alkalis, and the products of their mutual action, *i.e.* salts. Closely allied to, and sometimes regarded as identical with, the alkalis, was the group of earths. These bodies were known to neutralise acids and affect colouring matters like alkalis, but they were much less soluble in water than the alkalis. It was taught by some chemists that an alkali is hidden in every earth, and by others that an alkali is an earth refined by the presence of acid and combustible matter. Black's exact quantitative investigations tended to disparage all such explanations as these; but it yet remained to find the precise composition of the alkalis and the earths. Lavoisier thought that these bodies must be compounds; but, as he had no means of proving this, he classed them with the elements, while suggesting that the earths were probably compounds of oxygen with unknown metals. In 1807 Davy decomposed two alkalis, potash and soda, by passing an electric current through these substances when molten; and a year later he succeeded, by the same agency, in separating the earthy bodies lime, baryta, and strontia, into oxygen and, in each case, a metal.

The name alkali is now generally applied to the compounds of hydrogen and oxygen with one or other of the five metals, lithium, sodium, potassium, rubidium, cæsium (*v.* ALKALIS, METALS OF THE); an aqueous solution of ammonia is also regarded as containing an alkali, viz. a compound of hydrogen and oxygen with the radicle *ammonium* (*v.* AMMONIUM COMPOUNDS). The alkalis are classed with the hydroxides, *i.e.* compounds of hydrogen and oxygen with a third element, rather than with the hydrates, *i.e.* compounds of water with an oxide or a salt (*v.* HYDRATES). The general formula of the alkalis is written MOH rather than M_2OH_2O; M = Li, Na, K, Cs, Rb, or NH_4. The alkalis are very soluble in water; these solutions neutralise acids forming salts, and also precipitate most of the heavy metals from their solutions in the form of oxides or hydrated oxides; aqueous solutions of the alkalis act corrosively on animal and vegetable substances, and also alter the tint of many colouring matters. When moist, the alkalis, with the exception of ammonia, readily combine with carbonic acid to form carbonates. Lithia is much less soluble in water than the other alkalis. The solid alkalis are not decomposed by the action of heat alone.

M. M. P. M.

ALKALI-BLUE *v.* PHENYL-ROSANILINE SULPHONATE OF SODA.

ALKALIMETRY.—The estimation of alkalis by volumetric methods, *v.* ANALYSIS.

ALKALINE EARTHS, METALS OF THE. —CALCIUM, STRONTIUM, BARIUM.—Certain substances, more or less alkaline in their properties, but differing from alkali chiefly in being insoluble in water, were known from early times; these substances were called earths. After a time some of the earths were found to dissolve in water, although to a less extent than alkalis; these comparatively soluble earths were separated from the others and classed together as the alkaline earths. The best known alkaline earth is lime; this substance was long considered identical with baryta and strontia, but in 1774 Scheele proved that baryta was different from lime, and in 1792 Hope distinguished strontia from the two other alkaline earths. After decomposing the alkalis potash and soda, Davy applied the agency of electricity to the three substances just named, and in 1808 he succeeded in separating each into oxygen and a metal. Davy made his experiments quantitative; he also synthesised the three alkaline earths from oxygen and the metals he had himself discovered; thus he proved the alkaline earths to be metallic oxides. The metals calcium, barium, and strontium were not obtained in a state of approximate purity until 1855. The metal magnesium is sometimes classed with calcium, barium, and strontium; but, on the whole, it seems better to place magnesium with zinc and cadmium (*v.* p. 114, also MAGNESIUM GROUP OF METALS).

Some of the principal data regarding the metals of the alkaline earths are presented in the following tables.

	Calcium	Strontium	Barium
Atomic weights	39·9	87·3	136·86

No compounds gasified. Combining weights determined; and most probable formulæ of oxides and chlorides deduced from considering analogies with other oxides, &c. Molecular weights unknown.

Melting points (data uncertain)	high red-heat above strontium	moderate red-heat above barium	below red-heat
Specific gravities (approximate)	1·58	2·5	3·75
Specific heats	0·17	not determined	not determined
$\frac{\textit{Atomic weight}}{\textit{Spec. grav.}}$	25·3	34·9	36·5
Heats of formation in aqueous solutions (Thomsen).			
(1) Of haloid salts:			
$[M,Cl^2,Aq]$	187,600	195,700	196,800
$[M,Br^2,Aq]$	165,800	173,800	174,900
$[M,I^2,Aq]$	135,000	143,400	144,500
(2) Of oxides:			
$[M,O,Aq]$	149,260	157,780	158,760
(3) Of hydroxides:			
$[M,O^2,H^2,Aq]$	217,620	226,140	227,120
Heats of hydration (Thomsen).			
(1) Of haloid salts:			
$[MCl^2,6H^2O]$	21,750	18,640	$[BaCl^2,2H^2O]$ 7,000
$[MBr^2,6H^2O]$	25,600	23,330	$[BaBr^2,2H^2O]$ 9,110
(2) Of oxides:			
$[MO,H_2O]$	15,540	17,700	22,260
Heats of neutralisation of oxides in solution (Thomsen):			
$[MOAq,H^2SO^4Aq]$	31,150	31,150	31,150
$[MOAq,H^2Cl^2Aq]$ } $[MOAq,H^2N^2O^6Aq]$ }	27,640	27,640	27,640

	Calcium	Strontium	Barium
Malleability, colour, &c.	Very ductile, but when hammered becomes brittle; whitish-yellow; hardness about same as lead.	Ductile and malleable; colour resembles calcium but clearer; harder than lead.	Somewhat ductile; gold-yellow colour.
Wave-lengths of most characteristic lines in spectra.	Ca_β (yellow) 5588. H (violet) 3969. K (do.) 3933·8.	Sr_δ (blue) 4604	Ba_γ (yellow) 5538.
Chemical properties.	Quickly oxidises in moist air; decomposes cold water rapidly; heated to redness in air, burns without smoke; readily combines with Cl, Br, I, P, and S, at high temperatures.	Closely resembles calcium; decomposes water more rapidly.	Resembles calcium; burns when heated in O–H flame.
Occurrence and preparation.	Very widely diffused in rocks, waters, plants, and animals, as carbonate, sulphate, phosphate, and silicate: prepared by electrolysis of mixture $CaCl_2$, $SrCl_2$, and NH_4Cl.	Not very widely diffused; occurs as carbonate and sulphate in rocks, and waters; prepared by electrolysis of fused $SrCl_2$.	Not very widely diffused; occurs as carbonate, sulphate, and silicate, in rocks, waters, and certain plants: prepared by electro-[illegible]is of $BaCl_2$ mixed [illegible]H_4Cl.

un affected the colour of many | molten; and a year later he succeeded ...

General Formulæ and Character of Salts.

MO, MO_2, MO_2H_2, MS, MS_2H_2, MX_2(X = Cl, Br, I, F, CN), MSO_4, $M2NO_3$, MCO_3, &c., where M = Ca, Sr, or Ba. MO_2 decomposed by heat. Salts for the most part white; no great tendency to form double salts; polysulphides known, $SrS_4 6H_2O$ and BaS_4H_2O, in definite crystals. Oxides and hydroxides markedly basic; latter, except that of Ba, decomposed by heat alone into oxides and water; almost all similar salts isomorphous; many salts isomorphous with corresponding compounds of Mg, *e.g.* carbonates; most, with corresponding compounds of lead; MO and MO_2H_2 not very soluble in water, solubility increases as atomic weight of metal increases; MCl_2 and MBr_2 easily soluble, solubility decreases as atomic weight of metal increases; $CaSO_4$ very slightly soluble (S. ·272 at 38°), $SrSO_4$ nearly insoluble (S. ·01 at 100°), $BaSO_4$ insoluble. $CaCO_3$ slightly soluble (S. 1·13 at 100°), $SrCO_3$ and $BaCO_3$ nearly insoluble. Nitrates all soluble, solubility decreases as atomic weight of metal increases; $Ca2NO_3$ S. 93·1 at 0°. $Sr2NO_3$ S. 54·9 at 10°. $Ba2NO_3$ S. 7 at 10°.

These data show that the metals of the alkaline earths differ from the alkali metals (compare data for latter on p. 115); the former are not so readily oxidised as the latter; the heats of formation of the oxides of the alkaline earth metals are smaller than those of the alkali metals; the hydroxides of the alkali metals cannot, but the hydroxides of the alkaline earth metals except that of Ba can, be separated into oxides and water by the action of heat alone. The alkali metals are specifically lighter than those of the alkaline earths; the composition of the oxides and chlorides of the former is represented by formulæ containing two atoms of metal to one of oxygen or two of chlorine, while that of the corresponding salts of the latter is represented by formulæ containing one atom of metal to one of oxygen or two of chlorine. The salts of the alkali metals, as a class, are much more soluble in water than those of the alkaline earth metals; the hydroxide, carbonate, and phosphate of lithium are, however, considerably less soluble than the corresponding salts of the other alkali metals (*v.* ALKALIS, METALS OF THE, p. 115). Although magnesium forms the oxide MgO, the chloride $MgCl_2$, and the sulphate $MgSO_4$, salts analogous in composition to the oxides, chlorides, and sulphates of the metals of the alkaline earths, nevertheless this metal is clearly cut off from these by the following, among other, characteristics. The heats of formation, in aqueous solutions, (1) of the haloid salts of Ca, Sr, and Ba, (2) of Mg, Zn, and Cd, indicate the existence of two groups, in the first of which (Ca, Sr, Ba) the value of the reaction increases, and in the second of which (Mg, Zn, Cd) the value of the reaction decreases, as the atomic weights of the metals increase. The data are from Thomsen:

M	[M, Cl², Aq]	[M, Br², Aq]	[M, I², Aq]
Ca . . .	187,600	165,800	135,300
Sr . . .	195,700	173,800	143,400
Ba . . .	196,300	174,400	144,000
Mg . . .	186,900	165,000	134,600
Zn . . .	112,800	90,900	60,500
Cd . . .	96,300	74,400	44,000

Magnesium is scarcely oxidised in ordinary air; it does not decompose cold water; nor does it combine so readily with the halogens as the metals of the alkaline earths do. The spectrum of magnesium, as produced in the electric arc, is marked by a series of triplets alternately sharply marked and diffuse, and diminishing in brightness towards the more refrangible side; the spectra of barium and strontium show no triplets, but a series of lines only; the spectrum of calcium is marked both by lines, perhaps homologous with those of barium and strontium, and also by well-marked triplets (Liveing and Dewar). Magnesium sulphate is very soluble in water; this salt, and also the carbonate and chloride, readily combines with salts of the alkali metals to form double compounds. Magnesium oxide is scarcely if at all soluble in water; the formation of the hydroxide by the action of water on the oxide is attended with the production of very little heat: $[MgO, H^2O] = $ (approx.) 3,000 (Thomsen).

The mutual relations of the two groups of elements—the alkaline earth metals and the magnesium metals—are suggested by the position they occupy in the classification based on the *periodic law* (*q. v.*; *v.* also CLASSIFICATION). Both belong to Group II.; but Ca, Sr, and Ba occur, along with Be, in even series, and Mg, Zn, and Cd, along with Hg, in odd series, of that group. The metal beryllium exhibits analogies both with the alkaline earth, and with the magnesium, metals; it is one of those elements called '*typical*' by Mendeléeff (*v.* BERYLLIUM). For accounts of the metals of the alkaline earths and their binary compounds *v.* the articles BARIUM, CALCIUM, and STRONTIUM; and for the other salts of the metals *v.* CARBONATES, NITRATES, SULPHATES, &c.

M. M. P. M.

ALKALIS, METALS OF THE. (LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, CÆSIUM.)—The history of the name *alkali* has been briefly traced in the article under that heading. The alkalis potash and soda were decomposed by Davy in 1807; lithia (discovered by Arfvedson in 1817) was decomposed by the same chemist about 1818; cæsia and rubidia were discovered by Bunsen and Kirchoff in 1860–61, rubidium being obtained in the same year by Bunsen, by electrolysing the chloride; approximately pure cæsium was not prepared until 1882, in which year Setterberg obtained the metal by electrolysing the double cyanide of cæsium and barium. The more important properties of these metals and of their principal salts are presented in the tables on the next page and page 116.

Thermal values of reaction with water.—When an alkali metal reacts with water an alkaline hydroxide is formed and dissolved, and hydrogen is evolved; thus:—

$$M_2 + xH_2O = 2MOHAq + (x-2)H_2O + H_2.$$

This reaction would be expressed in the notation of thermal chemistry thus:—

$$[M^2,2H^2O] = -2[H^2,O] + [M^2,O^2,H^2,Aq].$$

The value of $2[H^2,O]$ is 136,720 gram-units when H_2O represents 18 grams liquid water; when the value of $[M^2,O^2,H^2,Aq]$ considerably

	Lithium	Sodium	Potassium	Rubidium	Cæsium
Atomic weights .	7·01	23	39·04	85·2	132·7

No compounds gasified. Combining weights determined; and most probable formulæ of oxides and chlorides deduced by chemical methods from considering smallest masses of these salts which take part in chemical changes. Molecular weights unknown.

Melting points .	180°	95°·5°	58°–62°	38°	26°–27°
Specific gravities .	0·59	0·98	0·87	1·52	1·88
Specific heats .	0·94	0·29	0·17	not determined	not determined
$\frac{\textit{Atomic weight}}{\textit{Spec. grav.}}$.	11·9	23·5	44·9	56·1	70·6

Heats of formation in aqueous solutions (Thomsen).

(1) of haloid salts:

$[M^2,Cl^2,Aq]$ . .	204,500	193,000	202,300	—	—
$[M^2,Br^2,Aq]$ . .	182,600	171,200	180,500	—	—
$[M^2,I^2,Aq]$ . .	152,200	140,600	150,000	—	—

(2) Of oxides and hydroxides:

$[M^2,O,Aq]$ . .	166,500	155,300	164,600	—	—
$[M^2,O^2,H^2,Aq]$ . .	234,900	223,600	232,900	—	—

Heats of neutralisation of oxides in solution (Thomsen):

$[M^2OAq,H^2SO^4Aq]$.	31,150	31,150	31,150	—	—
$[M^2OAq,H^2Cl^2Aq]$ } $[M^2OAq,H^2N^2O^6Aq]$ }	27,640	27,640	27,640	—	—

exceeds 136,720, we should expect the metal M to decompose liquid water. Thomsen has determined these values:—

M	$[M^2,O^2,H^2,Aq]$.
$M = Li_2$	234,900
Na_2	223,600
K_2	232,900

General formulæ and characters of salts.—M_2O, (M_2O_2, M_2O_4), MOH, M_2S, (M_2S_2, M_2S_5), MSH, MX($X = Cl$, Br, I, F, CN), M_2SO_4, $MHSO_4$, MNO_3, M_2CO_3, $MHCO_3$, &c., where M = Li, Na, K, Rb, or Cs. No oxides or sulphides of Rb and Cs have been prepared in a state of purity. Li_2O is the only oxide, and Li_2S the only sulphide, of Li known with certainty. Na_2O_2 and K_2O_4 are very stable towards heat, but quickly decompose in moist air, giving off oxygen and forming NaOH and KOH. Salts for the most part white, and very soluble in water; but LiOH is much less soluble than the other hydroxides, and Li_2CO_3 and Li_3PO_4 than the other carbonates and phosphates—(Li_2CO_3, S. ·769 at 13°, S. ·778 at 100°; Li_3PO_4, S. ·04 at 18° [approx.].) Chlorides, except LiCl, form many double salts with chlorides of heavy metals, *e.g.* M_2PtCl_6, $SbCl_3 6MCl$, &c. Sulphates, except Li_2SO_4, form alums, also double salts with sulphates of magnesium group. Most salts are isomorphous, but some of the lithium salts are not strictly isomorphous with corresponding salts of the other metals; some compounds of silver and thallium are isomorphous with those of the alkali metals. All the metals of this group are electropositive towards any other elements; their oxides and hydroxides are strongly basic. The latter cannot be decomposed by heat alone into oxides and water. Lithium differs from the other members of the group in the comparative insolubility in water of its hydroxide, carbonate, and phosphate, in the non-formation of an alum, and in some other respects (compare heats of formation of analogous salts); this element serves to connect the group of the alkali metals with that of the metals of the alkaline earths in somewhat the same way as the latter group is connected with zinc and cadmium by the element magnesium (*v.* Alkaline earths, Metals of the). The metals copper and silver are to some extent connected with the alkali metals. Copper forms two series of salts represented by Cu_2O and CuO respectively; the former, so far as composition goes, are analogous to the alkali salts. They are, however, much more insoluble in water than these, and, with the exception of the iodide and cyanide and some double salts, are much less stable than the salts formed from the oxide CuO. The salts of silver, as a class, are much less soluble in water than those of the alkali metals; their composition is similar—Ag_2O, $AgNO_3$, Ag_2SO_4, &c.; some of them are isomorphous with corresponding sodium salts, *e.g.* Ag_2SO_4. Silver forms an alum, and its oxide is markedly basic.

The alkali metals are placed in Group I., according to the classification of elements based on the periodic law, and this group also contains the metals Cu, Ag, and Au. Li, K, Cs, and Rb belong to even series, and Na, Cu, Ag, and Au, to odd series, of Group I. There can be no doubt, however, that sodium is closely connected with the other alkali metals, and that the three heavy metals (Cu, Ag, Au) present only feebly marked analogies to each other, and to the metals of the alkalis. In considering the classification of elements which the periodic law presents, attention must be paid, not only to the group in which any given family of elements occurs, but also to the character of the elements which precede and those which

follow the given family in the same series; the position of the family in the complete scheme must also be considered (v. PERIODIC LAW).

In some respects thallium exhibits a marked chemical resemblance to the alkali metals; it forms an oxide Tl_2O and a hydroxide TlOH, both of which dissolve in water, producing a strongly alkaline and basic liquid, marked by most of the properties which characterise aqueous solutions of soda and potash; it also forms salts—Tl_2CO_3, Tl_2SO_4, $TlNO_3$, &c.—which, as a class, are easily soluble in water, and many of which are isomorphous with the corresponding alkali salts. Some of the thallous salts, however, resemble those of lithium in being comparatively insoluble, *e.g.* TlCl and Tl_3PO_4. Thallium also forms an alum, and a double platinum chloride Tl_2PtCl_6. On the other hand, the metal itself differs much from the alkali metals; it is heavy, is not very easily

	LITHIUM	SODIUM	POTASSIUM	RUBIDIUM	CÆSIUM
Malleability, colour, &c.	Silver-white; easily drawn into wire, but less tenacious than lead; very soft, may be welded at ordinary temperature; not volatile at red heat.	Silver-white; soft as wax at ordinary temperature; very ductile at 0°; can be distilled at red heat.	White; brittle at 0°, malleable at 5° or so, pasty at 15°: can be distilled at 700°-800°.	Silver-white; soft as wax at −10°.	Silver-white; soft at ordinary temperature.
Wave-lengths of most characteristic lines in spectra.	Li_α (red) 6705 (blue) 4602	D_1 (orange) 5895 D_2 (orange) 5889	(yellow) 5800 K_β (violet) 4044	Rb_γ (red) 7800 Rb_α (orange) 6297	Cs_β (blue) 4597 Cs_α (blue) 4560
Chemical properties.	Oxidises in ordinary air but not so rapidly or completely as other metals of the group; decomposes cold water rapidly but without itself melting; ignites at temperature much above its melting-point; readily combines with halogens and sulphur.	Oxidises rapidly in air; decomposes water rapidly; combines very energetically with halogens and sulphur, decomposes many haloid salts at high temperatures.	Oxidises very rapidly in air; decomposes water rapidly; combines with halogens and sulphur.	Oxidises in air so rapidly that usually takes fire; decomposes water most rapidly; burns brilliantly in vapours of halogens, sulphur, and arsenic.	Exceedingly easily oxidised. Properties not yet exactly studied. Most electropositive of all elements.
Occurrence and preparation.	Widely diffused in rocks, waters, plants, and some animal secretions; occurs as silicate and phosphate with other alkali metals; prepared by electrolysis of mixture of LiCl and NH_4Cl.	In large quantities as chloride, silicate, fluoride, nitrate, &c., prepared by deoxidising Na_2CO_3 by hot carbon.	In large quantities as nitrate, silicate, sulphate &c.; prepared as Na.	Very widely diffused, but in very small quantities; in most K and Na minerals; in waters; no special Rb mineral known; prepared as Na and K	As silicate in a rare mineral. In minute quantities in many rocks and waters; prepared by electrolysis of double cyanide of Cs and Ba using Al poles.

oxidised, does not decompose water except at a red heat, and is much more electro-negative than the alkali metals. Thallium forms an oxide, Tl_2O_3, from which a series of salts—$Tl_2 3SO_4$, $TlCl_3$, &c.—is obtained; these salts exhibit analogies with those of the earth metals. The heats of formation of thallous oxide, hydroxide, and chloride, are much smaller than those of the alkali salts; Thomsen gives these numbers: $[Tl^2,O,Aq] = 39,200$; $[Tl^2,O^2,H^2,Aq] = 107,500$; $[Tl^2,Cl^2,Aq] = 76,900$ (v. EARTHS, METALS OF THE, and THALLIUM).

An aqueous solution of ammonia is strongly alkaline; when neutralised by acids salts are obtained which, as a class, closely resemble those of the alkali metals, with which they are, for the most part, isomorphous. These salts are considered to be compounds of the radicle ammonium (NH_4) with acid radicles; the general formulæ given for salts of the alkali metals apply to the ammonium salts if M be taken to represent NH_4. This radicle ammonium replaces the elements Li, Na, K, Rb, or Cs, in most compounds without altering the crystalline

form, and without changing the chemical type, of these compounds. The salts of ammonium are, therefore, classed with those of the alkali metals. (For more details regarding the constitution of these salts, and for an account of their properties, see AMMONIUM COMPOUNDS.) For accounts of the individual alkali metals and their binary compounds, see the articles CÆSIUM, LITHIUM, POTASSIUM, RUBIDIUM, and SODIUM; and for the other salts of these metals see CARBONATES, NITRATES, SULPHATES, &c.

M. M. P. M.

ALKALIS, Action on Organic Compounds. The tendency of alkalis is to form salts. Thus they react with acids and other hydroxylic compounds by displacing the hydrogen by potassium or sodium (p. 53). Neutral substances are frequently saponified by alkalis, *i.e.* turned into salts. Saponification means soap-making; in the narrowest sense it means boiling a fat with potash or soda: $C_3H_5(OC_{18}H_{35}O)_3 + 3KOH = C_3H_5(OH)_3 + 3KOC_{18}H_{35}O$. In a broader sense it means the splitting up of any compound ether into its alcohol and its acid, whether by means of an alkali, an acid, or by water alone. In the broadest sense it means the conversion of a neutral substance into an acid or the salt of an acid. Alkalis saponify compound ethers, nitriles, amides, and amic acids. In the case of nitriles the reaction takes place as follows: $R.CN + KOH + H_2O = R.CO_2K + NH_3$. Alkalis act upon chlorinated or brominated substances with production of haloid salts: the reaction is either one of substitution; $CH_3Cl + KOH = CH_3.OH + KCl$: or else HCl or HBr is abstracted; $CH_2Br.CH_2Br + KOH = CH_2{:}CHBr + KBr + H_2O$. The latter equation represents the action of alcoholic KOH on chlorinated or brominated hydrocarbons. Hydrogen and halogen are always taken from contiguous carbon atoms. Alcoholic potash sometimes displaces halogen atoms by ethoxyl: $CH_2Cl.CO_2K + KOH + EtOH = CH_2(OEt).CO_2K + KCl + H_2O$. γ-Chloro-acids are converted by neutralisation with potash into lactones (*q. v.*). When the halogen is in place of hydrogen in the benzene nucleus, it cannot be turned out by aqueous potash unless a nitro-group is also present. Thus chloro-benzene is not affected by potash, while *o*- and *p*- chloro-nitro-benzenes are converted into nitro-phenols.

When phenol is boiled with chloroform and NaOHAq, oxy-benzoic aldehyde results (Tiemann a. Reimer's reaction): $C_6H_5ONa + 3NaOH + CHCl_3 = C_6H_4(ONa)COH + 3NaCl + 2H_2O$ (*B.* 9, 824).

By the same method the group CHO can be introduced into many derivatives of phenol (p. 109).

If tetrachloride of carbon be used instead of chloroform, carboxyl enters the phenol, forming a carboxylic acid: $C_6H_5ONa + 5NaOH + CCl_4 = C_6H_4(ONa).CO_2Na + 4NaCl + 3H_2O$. Alcoholic potash sometimes acts as a reducing agent (p. 99, l. 42).

Potash-fusion (*or soda fusion*).

1. Converts aromatic sulphonates into phenols:

$$C_6H_5.SO_3K + KOH = C_6H_5OH + K_2SO_3.$$

2. Displaces halogens by hydroxyl:

$$C_6H_4Cl.CO_2K + KOH = C_6H_4(OH).CO_2K + KCl.$$

However, owing to the high temperature required, a subsequent migration of the hydroxyl sometimes takes place. Thus when any halogen benzene sulphonate or halogen phenol is fused with potash at 235°–270°, resorcin is produced.
3. Converts carboxylates into hydrocarbons: $CH_3.CO_2K + HOK = CH_4 + CO_3K_2$. Soda-lime, lime, or baryta may also be used for this purpose.
4. Converts the higher fatty aldehydes and aromatic aldehydes into alcohol and salt of the acid: $2Ph.CHO + KOH = Ph.CO_2K + Ph.CH_2OH$. In other cases also, potash acts by oxidising one portion of the substance and reducing another. Thus glycerin distilled with potash gives (*a*) by reduction, propylene glycol, (*b*) by oxidation, potassic acetate and formate. Similarly anthraquinone sulphonate gives (*a*) by reduction, anthracene, (*b*) by oxidation, alizarin.
5. Splits up unsaturated acids at the point of non-saturation into two salts:

$$CH_3.CH{:}CH.CO_2H + 2KOH = 2CH_3.CO_2K + H_2.$$

6. Resins usually give *p*-oxy-benzoate protocatechuate, and phloroglucin.

ALKALOIDS.—The term alkaloid was first applied to any organic base. It is now usually restricted to organic bases that are of vegetable origin and produce marked toxicological effects. Thus such bodies as ethylamine, asparagine, and leucine, are not usually classed as alkaloids. All the alkaloids contain nitrogen, and all except coniine, nicotine, and sparteïne contain oxygen. These three alkaloids are volatile, the others are fixed. The vegetable alkaloids are ammonia-, not ammonium-, bases, that is, they combine with HCl without elimination of H_2O. The following alkaloids have been described:

From *Achillea Moschata*: achilleïne, moschatine.

From *Aconitum Napellus, ferox, &c.*: aconitine, picro-aconitine, pseudo-aconitine, japaconitine, lycaconitine, myoctonine.

From *Æthusa Cynapium*: cynapine.

From *Agaricus*: agarythrine.

From *Alstonia constricta*: alstonine, porphyrine, alstonidine, alstonicine.

From *Arariba rubra*: aribine.

From *Artemisia abrotanum*: arbrotine.

From *Aspidosperma*: aspidospermine, aspidospermatine, aspidosamine, hypoquebrachine, quebrachine, quebrachamine, paytine, paytamine.

From *Angustura bark*: cusparine, gasipeïne.

From *Atherosperma*: atherospermine.

From *Atropa*: atropine, hyoscyamine, hyoscine, belladonine.

From *Baccharis*: baccharine.

From *Baptisia tinctoria*: unnamed.

From *Bebeeru*: beberine.

From *Berberis*: berberine, oxyacanthine, hydrastine.

From *Buxus*: buxine, buxidine.

From *Calabar beans*: physostigmine or eserine.

From *Capsicum*: capsicine.

From *Cannabis indica*: an unnamed alkaloid (M. Hay, *Ph.* [3] 13, 998).

From *Chelidonium*: chelerythrine, chelidonine.

From *Cinchona*: quinine, cinchonine, conquinine, quinicine, homoquinine, hydroquinidine, cinchonidine, aricine, cusconine, cusconidine, cincholine, cuscamine, cuscamidine, quinamine, cinchamidine, cinchotine, hydrocinchonine, con-

quinamine, hydroquinine, dicinchonine, dicon-quinine, javanine, paricine.

From *Coca leaves*: cocaïne, ecgonine, hygrine.

From *Cocoa beans*: theobromine.

From *Coffee berries*: caffeïne.

From *Colchicum*: colchicine.

From *Conessi bark*: conessine.

From *Conium*: coniine.

From *Corydalis*: corydaline.

From *Crossoptera*: crossopterine.

From *Curare*: curarine.

From *Cytisus*: cytisine.

From *Delphinium*: delphinine, delphinoidine, delphisine, staphisagrine.

From *Dita bark*: ditamine or ditaïne, echitamine, echitenine.

From *Duboisia*: duboisine or hydrocyamine.

From *Ergot*: ergotine.

From *Erythrophleum*: erythrophleïne.

From *Esenbeckia*: esenbeckine.

From *Fraxinus americana*: an unnamed alkaloid (F. B. Power, *Ph.* [3] 12, 812).

From *Fumaria*: fumarine.

From *Gelsenium*: gelsenine.

From *Geselmium*: geselmine.

From *Glaucium*: glaucine, glaucopicrine.

From *Harmala*: harmaline, harmine.

From *Humulus lupulus* (*Hops*): lupuline (hopeïne), neurine.

From *Hymenodictyon*: an unnamed alkaloid.

From *Ipecacuanha*: emetine.

From *Isopyrum*: isopyrine, pseudo-isopyrine.

From *Lobelia*: lobeline.

From *Lotur bark*: loturine, colloturine, loturidine.

From *Loxopterygium*: loxopterygine.

From *Lupinus*: lupinine, lupinidine.

From *Lycopodium*: lycopodine.

From *Macleya*: mackleyine, sanguinarine.

From *Menispermum*: menispermine.

From *Mustard*: sinapine.

From *Nicotiana tabacum*: nicotine.

From *Nymphæa alba*: an unnamed alkaloid (Grüning, *B.* 16, 969).

From *Oleander*: oleandrine.

From *Opium*: morphine, codeïne, thebaïne, papaverine, narcotine, narceïne, hydrocotarnine, pseudomorphine, codamine, laudamine, laudanosine, meconidine, lanthopine, protopine, cryptopine, crytopine, oxynarcotine.

From *Papaver rhœas*: rhœadine.

From *Papaver somniferum*: *v.* Opium.

From *Pennius*: boldine.

From *Piper nigrum* (*Pepper*): piperine.

From *Pereiro bark*: geissospermine, pereirine.

From *Pilocarpus leaves*: pilocarpine, jaborine, pilocarpidine.

From *Pomegranate bark*: pelletierine.

From *Poppy*: rhœadine. *Opium Poppy v. Opium.*

From *Ratany root*: ratanhine.

From *Ricinus* (castor-oil plant): ricinine.

From *Salamandra*: samandrine.

From *Saphora*: saphorine.

From *Sinapis*: sinapine.

From *Spartium*: sparteïne.

From *Strophantus*: strophantine.

From *Strychnos*: strychnine, brucine.

From *Thalictrum*: thalictrine.

From *Taxus*: taxine.

From *Tea leaves*: caffeïne.

From *Tobacco*: nicotine.

From *Trigomella*: trigomelline, neurine.

From *Veratrum*: veratrine, veratridine, cevadine, cevadilline, jervine, rubijervine, pseudojervine, veratralbine.

From *Vetch*: vicine.

Formation of alkaloids in plants. Most of the above alkaloids are pyridine derivatives. They are probably produced by the action of ammonia or amido compounds upon non-nitrogenous bodies. Pechmann a. Welsh (*B.* 17, 2384) consider that the non-nitrogenous bodies are such acids as meconic, chelidonic, and cumalic, which are probably furfurane derivatives. These three acids are converted by ammonia into oxypyridine carboxylic acids. Cumalic acid is formed artificially from malic acid by action of conc. H_2SO_4; and it is probable that the two other acids are also formed by condensation of simpler acids.

V. Meyer has suggested that hydroxylamine by acting upon aldehydes may also play some part in the production of the nitrogenous constituents of plants.

Extraction: The tissue is extracted with dilute acid and the extract ppd. by ammonia, potash, soda, lime, or magnesia. Volatile alkaloids are then distilled, fixed alkaloids are crystallised from a suitable solvent. The extraction of alkaloids from animal matter, as in cases of poisoning, is described in the next article.

Reactions.—1. *Sodic phosphomolybdate* added to solutions acidified with nitric acid gives, in the cold, a yellowish-white flocculent pp. Aniline, the alkylamines, and quinoline, as well as silver, mercurous, and lead, salts are also ppd. by this reagent (Sonnenschein, *A.* 104, 45). To recover the alkaloid, the pp. is boiled with baryta, when volatile alkaloids distil over. The residue is saturated with CO_2, evaporated to dryness and extracted with alcohol. Sonnenschein's reagent is prepared by dissolving yellow ammonic nitro-molybdate in Na_2CO_3Aq, drying and strongly heating; if reduction of molybdic acid take place, the product is moistened with HNO_3 and again heated. It is then heated with water, nitric acid is added, and the liquid diluted until 10 parts of the solution contain 1 part of solid residue.

2. *Phosphotungstic acid* may be used instead of phospho-molybdic acid (Scheibler, *Fr.* 12, 315; *J.* 1860, 157). The reagent, which is a mixture of sodic tungstate and phosphoric acid, is added to solutions acidified with H_2SO_4. *Phospho-antimonic acid* got by dropping antimonic chloride into aqueous phosphoric acid, precipitates morphine, narcotine, and nicotine, but not atropine (F. Schulze, *A.* 109, 177).

3. *Potassio-mercuric iodide* produces flocculent yellowish-white pps., insoluble in acids and in dilute alkalis, slightly soluble in excess of the reagent, easily soluble in alcohol, and generally also in ether (F. Mayer, *J.* 1863, 703; *A.* 133, 236; De Vrij, *J.* 1867, 602). Theobromine, caffeïne, glucosides, carbohydrates, and organic acids give no pp. with Mayer's solution. Albuminous and gelatinous substances, in presence of free acid (but not in alkaline solutions) give sticky pps. (Valser, *Fr.* 2, 79). To separate the alkaloid from the pp., the latter is triturated

with $SnCl_2$ and excess of aqueous KOH; this reduces the mercury to the metallic state, and the base is then extracted by its proper solvent.

Mayer's solution contains 13·5 g. mercuric chloride and 49·8 g. potassic iodide per litre.

4. *Potassio-bismuthous iodide* is prepared by dissolving $Bi(OH)_2NO_3$ (80 g.) in HNO_3 (200 c.c. of S.G. 1·18) and adding a conc. solution of KI (272 g.). The solution is cooled until KNO_3 crystallises, and the mother liquor is then diluted to a litre (Dragendorff, *Fr.* 5, 406; Kraut, *A.* 210, 310). The solution is added to the alkaloid dissolved in dilute H_2SO_4 or HI. Double iodides of the alkaloid and of bismuth are ppd. The alkaloid can be recovered by decomposing these double iodides with aqueous NaOH, and extracting with a proper solvent.

5. *Potassio-cadmic iodide* forms white flocculent pps. when added to solutions of alkaloids acidulated with H_2SO_4. The pps. soon become crystalline; they are soluble in alcohol, insoluble in ether. They dissolve in excess of the reagent. The alkaloid can be recovered by treatment with NaOHAq and a solvent (Marmé, *Bl.* [2] 9, 203).

6. *Potassio-platinic iodide* and *potassio-auric iodide* also pp. alkaloids (Selmi, *G.* 5, 255). These solutions are prepared by adding KI to solutions of $PtCl_4$ or $AuCl_3$ until the pp. first formed is redissolved. The platinum salt gives, in acetic acid solution, a black pp. with nicotine, but none with conessine; it also gives a wine-red pp. with solanidine but none with solanine. The gold salt gives, on evaporation, arborescent crystallisation with nicotine, but only oily drops with coniine.

7. A solution of iodine (1 pt.) in KI (1 pt.) dissolved in water (100 pts.) gives brown, often crystalline, pps. of the periodides. These polarise light like tourmaline. The alkaloids can be recovered by treating the pp. with SO_2Aq.

8. Animal charcoal removes most of the alkaloids from aqueous solution. The alkaloid can then be extracted from the charcoal by a suitable solvent (Graham a. Hofmann, *C. J.* 5, 173).

9. *Picric acid* pps. many alkaloids, even in presence of a large excess of H_2SO_4. Morphine, caffeïne, and glucosides are not so ppd. The reagent pps. English but not German preparations of atropine (Hager, *Fr.* 9, 110).

10. *Tannin* gives a white or yellowish-white pp. The salts of morphine, with the exception of the acetate in strong solution, are not ppd. by tannin. The alkaloids can be recovered by treating the pp. with lime.

11. *Platinic chloride* gives, in conc. solutions, a yellowish-white or yellow pp. *Chloride of gold* does the same (*cf.* Coninck, *Bl.* [2] 45, 131).

12. *Sodic nitroprusside* usually forms oily drops of the nitroprusside, which crystallises on standing (Horsley, *C. N.* 5, 355; E. W. Davy, *Ph.* [3] 11, 756).

13. The *electrolysis* of solutions of salts of alkaloids has been studied by Bourgoin (*Bl.* [2] 12, 438).

14. The alkaloids are ppd. by sodium salts of *glycocholic, hyoglycocholic,* and *taurocholic acids.* The pps. appear to be acid salts of the alkaloids (W. F. de l'Abre, *C. C.* 1872, 231).

15. *Hydric sulphide* passed into alcoholic solutions of alkaloids forms compounds containing sulphur (Palm, *J.* 1863, 433; E. Schmidt, *B.* 8, 1267).

16. The *absorption-spectra* of various alkaloids have been mapped by A. Meyer (*P.* [3] 13, 413).

17. A solution of *iodine monochloride* in HCl added to a solution of an alkaloid in HCl gives a pp., usually yellow and sparingly soluble (Tilden, *C. J.* 21, 145; Dittmar, *B.* 18, 1612; Ostermayer, *B.* 18, 2298). According to Dittmar, if the alkaloid contain one pyridine ring, the pp. is of the form XICl; if it contain two pyridine groups it is of the form YI_2Cl_2. However, NEt_4Cl, NEt_3HCl, caffeïne hydrochloride, and pyrrol, all give pps. though they contain no pyridine ring, while *B*-oxy-quinolines, and tetra-hydroquinoline give no such pps. The pps. may also be got by using a mixture of KI, KNO_2, and HCl, instead of ICl. The chloro-iodides are converted by excess of chlorine into unstable compounds $XICl_3$. Ammonia converts the chloro-iodides into iodo-amides, $XINH_2$; these are dark-green or dark-red unstable bodies, insoluble in water, but converted back into the chloro-iodides by HCl, and decomposed by boiling with alcohol according to the equation:

$$6XINH_2 = 3X + 3XI_2 + 4NH_3 + N_2.$$

These iodo-amides are also produced by the combination of the alkaloids with iodide of nitrogen.

Tests for alkaloids.—The above reactions are general. The following tests may be used in distinguishing the alkaloids from one another:—1. The alkaloid is *sublimed.* Sublimation begins below 100° in the case of caffeïne, theobromine, and cantharidine; between 150°-200° in the case of strychnine, morphine, and pilocarpine (Wynter Blyth, *C. J.* 33, 318). The following give no sublimate, but melt: (*a*) below 100° hyoscyamine, atropine; (*b*) between 100°-150° papaverine; (*c*) above 200° solanine. The sublimate is then examined microscopically (Helvig, *Fr.* 3, 43; Deane a. Brady, *C. J.* 18, 34).—2. Conc. H_2SO_4 produces colours with certain alkaloids, *e.g.* a blood-red colour with thebaïne and a crimson with veratrine.—3. Nitric acid usually produces a yellow solution, but morphine and brucine give a red colour.—4. Sulphuric acid containing a little molybdic acid, so-called sulphomolybdic acid, gives a violet colour with morphine, and characteristic colours with other alkaloids.—5. Erdmann's solution is prepared by adding HNO_3 (6 drops of S.G. 1·25) to water (100 c.c.) and adding ten drops of the diluted acid to 20 c.c. of conc. H_2SO_4. This solution gives a blue colour when warmed with solutions of codeïne, and characteristic colours with other alkaloids.—6. Chlorine water, followed by ammonia, gives a green colour with quinine, a red colour with narceïne, and an orange colour with narcotine.—7. A mixture of an alkaloid (1 pt.) with sugar (7 pts.) often gives colours with conc. H_2SO_4. Morphine and codeïne give a purple, aconitine a rose-red (R. Schneider, *P.* 147, 128).—8. H_2SO_4 and a little Ce_2O_3 give with strychnine a fine blue colour; with brucine, orange; narcotine, brown, cherry-red, finally wine-red; morphine, olive-brown, finally brown; codeïne, olive green, finally brown; quinine, pale yellow; cinchonine and caffeïne, no colour; veratrine,

atropine, solanine, emetine, brown; colchicine, green becoming brown; papaverine, almost black (Sonnenschein, *B.* 8, 632).

Optical Properties.—When the solution of an alkaloid affects a ray of polarised light the specific rotatory power of solutions of its normal salts is independent of the nature of the acid if the alkaloid is mono-acidic and the salt is not decomposed by water, but if the alkaloid is di-acidic the basic salts usually rotate much less than the normal salts (Oudemans, *R.* 1, 18).

ALKALOIDS, CADAVERIC *v.* PTOMAÏNES.

ALKALOIDS, POISONOUS, Detection and Estimation of.—This article will be directed to the simple detection of the chief alkaloids; but incidentally their quantitative estimation will be touched upon. The detection and complete recognition of an alkaloid by chemical tests is often a matter of great difficulty, even in the case of some well-known and potent alkaloids. Indeed, in some cases these difficulties are at present insurmountable by chemical means alone, and physiological experiments have to be called in aid. The obstacles to the recognition of these bases, when several are present, is still greater. Indeed, it may be stated that the complete separation of a mixture of commonly occurring alkaloids is a problem still awaiting solution. The toxicologist has too often to content himself with the identification of one or two alkaloids in organic mixtures, and the determination of their aggregate quantity, being unable to ascertain their individual amounts.

History.—The earliest methods devised for the detection of alkaloidal poisons in forensic research were those found effective for the separation of the vegetable alkaloids from the other matters with which they are found associated in nature; and modifications of these methods are even now employed for this purpose. The material to be operated on was extracted with diluted acids, aided by gentle heat, gummy and other substances removed by lead acetate, the excess of lead ppd. with hydrogen sulphide, and the alkaloid obtained as a salt—generally an acetate—in a greater or less degree of purity by evaporation of the solution. This and other crude processes were mostly abandoned when Stas (*A.* 84, 379) published his classical paper on the separation of alkaloids from organic mixtures, and devised a new and refined process, which was subsequently modified and improved by *Otto* (*A.* 100, 39), Dragendorff (*Gerichtl. chem. Ermit. v. Gift.*, 1876), and others. In one form or another, this process, generally known as that of Otto-Stas, is still the one most generally employed in forensic analyses, though Sonnenschein (*A.* 105, 45), Selmi (*C. J.* 1877, 93), and more recently L. Brieger (*Die Ptomaïne*, Pt. I., 1885; Pt. II., 1885; Pt. III., 1886) have each employed different but less refined methods for the general separation of the organic bases from the matters with which they are commonly associated.

Methods of Procedure.—If an apparently fairly pure solid body has to be examined, *e.g.* a crystalline medicinal powder, its alkaloidal nature may be demonstrated by ascertaining in the ordinary way that it contains both organic carbon and nitrogen; by its sparing solubility in aqueous alkaline, and its ready solubility in aqueous acid, solutions; and by adding to the acid solution reagents that react with the alkaloids as a class. The alkaloid will usually be ppd. from its acid or aqueous solution, if this be not too dilute, by caustic and by carbonated alkalis; and will appear either in the form of oily droplets (liquid and volatile alkaloids), or as an amorphous pp., becoming crystalline on standing. If the pp. redissolves in excess of the caustic alkali, as in the case of morphine, it will again separate when the alkali becomes carbonated, as by exposure to the air. Since none of the alkaloids are altogether insoluble in water, no pp. may form in very dilute solutions, and yet an alkaloid be present. There are, however, certain group reagents that pp. the alkaloids from their barely acid solutions, even when these are highly dilute; and these reagents are generally employed where the presence of an alkaloid is suspected. Such general reagents are the following; but it must be borne in mind that as any one of them may fail to give a precipitate with a given organic base, two or more of them must be used, under appropriate conditions, in order to prove or disprove the presence of an alkaloid in the solution to be tested.—1. A weak solution of *iodine in potassium iodide.* This reagent gives a more or less coloured pp. with extremely dilute solutions of most of the vegetable alkaloids.—2. *Bromine water* yields similar pps., but has the disadvantage of yielding pps. with the phenols also.—3. *Tannin* pps. most of the vegetable alkaloids from their not too dilute solutions.—4. *Mercuric chloride* in aqueous, and also in alcoholic solution, is a valuable pptant., and is especially useful in the separation of the organic bases resulting from putrefaction (*ptomaïnes*), for the separation of which the Otto-Stas method to be presently described is inadequate (L. Brieger, *op. cit.*).—5. *Potassio-mercuric iodide* solution is perhaps the most generally useful pptant. of the alkaloids; and from the ppts. thus produced the alkaloids may be recovered in a high state of purity by trituration with stannous chloride and solution of NaOH, and extraction of the alkaloid thus liberated, with ether.—6. *Phosphomolybdic acid* in nitric acid solution pps. the alkaloids from acid solutions. The alkaloids may be recovered from these pps. by decomposing them with barium hydrate, and either distilling off the alkaloid (volatile alkaloids), or after removing the baryta by means of a stream of carbon dioxide, subsequently extracting the alkaloid with absolute alcohol.—7. *Picric acid* is also a useful pptant., and from the pps. thus produced the alkaloids may be separated by acidification with HCl and agitation with ether.—Many other general pptants. of the alkaloids have been proposed, but the above fulfil almost every useful purpose; and on the ppn. of organic natural bases by alkalis, and their resolution and extraction by ether and other special solvents—or on their removal from organic solutions by one or other of the above pptants.—are based the most approved general methods for the separation of the poisonous alkaloids in forensic analysis.

The method most generally employed for the extraction of the vegetable alkaloids from admixture with animal matters is that originally devised by Stas for the separation of nicotine in

he course of a forensic analysis, and now known with modifications as the Otto-Stas method. The writer of this article has introduced further modifications which are embodied in the following description, and have been found by him necessary in those cases where unstable and easily hydrolysed alkaloids are to be sought for, such as morphine, which is readily decomposed by heating its acidified solutions, and aconitine, which is unstable in alkaline and especially in ammoniacal solutions. In all cases the method, which is a quantitative one, is greatly dependent for success upon the care with which the preliminary operations are conducted.

The organic material to be operated upon, if solid, is brought into as minute a state of division as its nature permits, and is then digested with twice its weight of rectified spirit of wine at a temperature of about 35°. Liquids are also treated with twice their volume of rectified spirit. Redistilled methylated spirit of wine may be used for these operations. After several hours' digestion the liquid is poured off from the deposited solids, and the digestion is repeated with a fresh quantity of spirit. This is again poured off, and mixed with the previous alcoholic infusion. If solid matter, *e.g.* liver, is operated on, the liquid is squeezed from the solid portion at each digestion in a piece of fine cambric which acts as a crude filter; and the liquids thus obtained are added to the other alcoholic liquids. After two or more digestions, according to the nature of the organic matter, the undissolved portions are subjected to a new digestion, also at 35°, with spirit faintly acidified with acetic acid. Some recommend tartaric in preference to acetic acid, but this is objectionable, when, as is usually the case, morphine has to be sought for: others use oxalic acid, but this acid may have to be sought for as well as the alkaloids. Enough acid must be added to keep the liquid just perceptibly acid, excess being avoided. After a prolonged digestion with the acidified alcohol, this is poured off, the solids squeezed, and the digestion repeated, but this time with unacidified spirit. A final digestion may be required, the rule being to continue the exhaustion with spirit of wine so long as any colour is imparted to this. The alcoholic liquids obtained before acidification after mixing are momentarily and rapidly raised to a temperature of 70°, cooled, and the insoluble residue filtered and washed with spirit; and those obtained with and after the use of acetic acid are similarly treated. But the two liquids, the unacidified and the acidified are not mixed till a later stage is reached. In this way, by keeping the liquids separate, danger of hydrolysation of unstable alkaloids is as far as possible avoided. The alcoholic infusions are now evaporated at a temperature never exceeding 35° to the consistency of a syrup. It is advisable during the course of the evaporations to neutralise a portion of the free acid with caustic soda from time to time, so as to keep the liquids just perceptibly acid. The evaporations are easily effected with tolerable rapidity by placing the liquids in shallow basins supported on large beakers some inches above the floor of an ordinary oven, which is heated by a gas flame playing on the top. The door is kept a little ajar. The advantages of this arrangement of the author's are, that overheating is avoided, evaporation is more rapid than by any other method, and all creeping of the liquids up the sides of the basins is obviated. This course of procedure is greatly preferable to distilling off and recovering the alcohol, as usually recommended. The syrupy liquid is now drenched with about 30 c.c. of absolute alcohol, with constant stirring or grinding in a mortar; the alcohol is poured off from the pasty mass which usually separates, and replaced by successive quantities of 15 c.c. alcohol so long as a colour is imparted to this. The alcoholic liquids are mixed, filtered, the filter washed with alcohol, and the filtrate evaporated in the oven, as before, at a temperature not exceeding 35°. The syrupy residues—that from the plain and that from the acidified spirit of wine—are diluted with a small quantity of water, filtered, the filters washed with water, and the filtrates mixed. They should, together, measure 15–20 c.c. The liquid is introduced into an accurately stoppered tube, partially neutralised, if necessary, with caustic soda, taking care, however, to leave it slightly acid. If the method laid down has been scrupulously followed, we have now a liquid containing the whole of the alkaloids, and free from albuminoids. The aqueous and faintly acid liquid in the tube is now covered with twice its volume of washed ether, and the whole is mixed by gently and repeatedly inverting the tube, care being taken not to emulsify the mixture by any violent agitation. The ether is allowed to separate, and this is favoured by giving an occasional sharp rotatory shake to the tube. The supernatant ether is then pipetted off, and replaced by a new and smaller quantity of ether. The tube is again shaken; and the operation of extraction with ether is continued till a few drops on evaporation leave no residue. Four or five extractions will generally suffice. The ethereal solutions as they are pipetted off are successively washed by vigorous shaking in a second stoppered tube with 5 c.c. water to which a few drops of dilute sulphuric acid have been added. The ether on evaporation may yield an oily residue which may be reserved for further examination and for physiological tests. But the acid liquid subjected to ethereal extraction will still contain nearly all the alkaloids, as the acid salts of these are mostly practically insoluble in ether; but the salts of some of the alkaloids being perceptibly soluble in ether may be met with in the 'acid-ether' extract. The acid aqueous solution, and the acidulated water with which the ether has been washed, are mixed, alkalised with sodium carbonate, and again exhausted four or five times as before with washed ether; only in this case the first exhaustion is made with a mixture of 1 vol. chloroform and 3 vol. ether, and the final extractions with ether alone. These successive ethereal extracts are washed in a tube by shaking anew with 5 c.c. water. They are then transferred to a third and finally to a fourth tube, the first containing 10 c.c. water acidulated with a few drops of sulphuric acid, and the last containing 5 c.c. water alone, and agitated. By these operations the alkaloids are first liberated from their salts by the alkali, then transferred to the ether-chloroform in which they are soluble; then

again converted into sulphates, which, being insoluble in ether and chloroform, again pass into the acid solutions, impurities being left behind in the ether. We have now again the alkaloids in acid solution, but in a much purer state than before. The acid liquid and the final wash-water are mixed, washed with a little ether once or twice, then re-alkalised with sodium carbonate, and well re-extracted with chloroform-ether and ether. These ethereal solutions are washed with water barely alkalised with sodium carbonate, then filtered through a dry filter, and evaporated to dryness in the oven below 35° in tared glass basins about eight centim. in diameter. Once dry, the residue may be transferred for a few minutes to the water-oven, dried at 100°, and weighed after cooling over sulphuric acid. This weight fairly represents that of the alkaloids. It is well before evaporating the bulk of the solution to evaporate a few c.c. only; if an oily odorous residue be left the presence of a volatile alkaloid is indicated; the evaporation is then modified by mixing the ether-chloroform with so much ether previously acidulated by agitation with a strong solution of hydrochloric acid as is necessary to render it acid. In this case it is not the free alkaloids, but their non-volatile hydrochlorides which are left and weighed. The residue may therefore be dissolved in water and subjected to appropriate tests—first for the alkaloids generally (*vide ante*), and secondly specifically for the volatile alkaloids. But if the solid free alkaloid has been obtained it must first be converted into a hydrochloride by moistening it with a very slight excess of very dilute hydrochloric acid, and evaporating to dryness *in vacuo* over sulphuric acid. The residue may then be dissolved in water and subjected to tests, which may be obtained from the ethereal extract either before or after conversion into hydrochloride and solution of this in water.

Morphine is practically insoluble in ether except immediately after ppn. from its solutions, hence if this alkaloid were present in the matters submitted to examination, but little of it would be removed by the chloroform and ether, more especially if, as is advisable, the agitation with these solvents was not executed immediately after the addition of sodium carbonate. In order to obtain the morphine, the *first* alkalised solution from which the other alkaloids have been removed must be re-extracted a few times with a well-washed mixture of equal volumes of acetic ether and ethyl ether, which is preferable to amyl-alcohol, and in which mixture morphine is soluble. The mixed ethers are washed with a little water, filtered through a dry filter, and evaporated just as the chloroform-ether was evaporated for the other alkaloids. The residue is usually not pure morphine, as acetic ether takes up other non-alkaloidal bodies, but these do not usually interfere with the morphine reactions.

G. Dragendorff (*Gerichtl. chem. Ermit. v. Gift.*, 1876, p. 141) has devised a process which proceeds upon the same general lines as that of Stas, but is much more elaborate. It requires, moreover, a higher temperature for the preliminary evaporation. The finely divided substance, if solid, is digested for several hours at a temperature of 40°–50° with dilute sulphuric acid—about 2 p.c. by volume of the acid. Liquids are acidulated with the same proportion of acid. The digestion is continued for several hours, and the mixture is then pressed, and filtered. The operation of extraction with dilute sulphuric acid is repeated two or three times, 100 c.c. of liquid being a convenient quantity for each extraction. The mixed filtrates, containing the alkaloids, are partially neutralised with magnesia, and carefully evaporated to a syrup at a temperature much below 100°; but never to dryness. It is certain that in this operation some alkaloids may be destroyed, and it is also asserted that basic bodies are formed by the decomposition of the albuminoids. A useful modification (L. Brieger, *op. cit.*) is to partially neutralise the liquid from time to time during the course of the evaporation, so that it is never more than very slightly acid in its reaction to litmus. The syrupy residue from the evaporation is mixed with three or four times its volume of rectified methylated spirit of wine, and a few drops of sulphuric acid, and allowed to digest at about 30° for twenty-four hours. The insoluble matter is separated by filtration and washed with spirit, and the filtrate and washings are distilled in a retort so as to recover the alcohol. The aqueous residue in the retort is diluted with water to 50 c.c., filtered, and introduced into a stoppered tube and exhausted successively with petroleum ether, benzene, and chloroform, 20–30 c.c. of each at a time, in the manner in which exhaustions are made with ether in Stas's process. The aqueous solution is then made alkaline with ammonia, and again exhausted successively with petroleum-spirit, benzene, chloroform, and amyl-alcohol. On evaporation of the respective solvents (consult what has been said under Stas's process as to volatile alkaloids) alkaloidal residues are obtained, which when taken up with water, either with or without previous conversion into hydrochlorides as necessity demands, may be submitted to appropriate tests for the alkaloids, and specially for the various suspected alkaloids.

Among the commoner alkaloids, and poisonous neutral substances:—

Petroleum ether removes from the acid aqueous solution:—some piperine, resins such as capsicin, camphor, and phenol.

Benzene further removes from the acid solution:—more piperine, caffeïne, colchicine, santonin, digitalin, cubebin, colocynthin, aloetin, picric acid, elaterin, and cantharidin.

Chloroform, again, removes from the acid aqueous solution: — cinchonine, theobromine, papaverine, narceïne, jervine, more digitalin, picrotoxin, smilacin, and senegin.

On rendering the solution alkaline with ammonia:—

Petroleum spirit removes from the alkaline solution:—strychnine, brucine, quinine, veratrine, aconitine, emetine, and the volatile alkaloids coniine, nicotine, lobeline, and trimethylamine (from putrefaction), the pimento-alkaloid, and aniline. If the presence of aconitine or emetine be suspected, the operation must be performed quickly, since these alkaloids rapidly decompose in alkaline solutions.

Benzene further removes from the alkaline solution:—atropine, hyoscyamine, physostig-

mine (eserine), thebaïne, codeïne, narcotine, and additional quantities of strychnine, brucine, quinine, cinchonine, veratrine, aconitine, and emetine.

Chloroform, again, removes from the alkaline solution:—some morphine, and additional quantities of cinchonine, narceïne, and papaverine.

Amyl-alcohol finally removes from the alkaline solution:—morphine, narceïne, and some neutral bodies, such as salicin.

Not all the substances enumerated above are poisonous; but they are bodies that may be present in medicinal mixtures, and hence are likely to come under the notice of the toxicologist in forensic analyses.

Selmi proposed another method of extracting the poisonous alkaloids, and applied it to the extraction of the ptomaïnes (*G.* 6, 153; *C. J.* 31, 93). The viscera are exhausted with alcohol and dilute sulphuric acid. This acidified alcoholic extract is filtered and evaporated at a temperature of 65°, again filtered, and evaporated to a syrup. The residue is taken up with water, filtered, the filtrate treated with basic lead acetate, and the mixture exposed to the air for twenty-four hours. It is then filtered, the excess of lead removed by hydrogen sulphide gas, and the filtrate concentrated. This is then repeatedly extracted with ether. The ethereal solution is then saturated with a stream of dry carbon dioxide gas, which generally causes a pp. of droplets containing some of the alkaloids, and adherent to the side of the vessel. The ethereal solution is poured off, mixed with about half its volume of water, and a current of carbon dioxide is again passed for twenty minutes, which may cause the ppn. of other alkaloids not ppd. by dry carbon dioxide. Usually the whole of the alkaloids are thrown down by these means, but if not, the ethereal solution is dehydrated by shaking with barium oxide, and then a solution of tartaric acid in ether is added to the clear liquid, taking care not to employ an excess of acid; any alkaloid that may remain in solution is thus thrown down. As a matter of precaution, the remains of the viscera or other matters operated on are mixed with barium hydrate and a little water, and agitated with pure amyl alcohol. The alkaloids may then be extracted from the alcohol by shaking it in a stoppered tube with very dilute sulphuric acid.

Sonnenschein (*A.* 104, 45) separates the alkaloids by ppn. with phosphomolybdic acid. In extracting the bases, the organic matter to be examined is repeatedly exhausted with very dilute hydrochloric acid, the mixed solutions filtered, and the filtrate evaporated in the oven at a temperature not exceeding 35° to a thin syrup; then diluted with water, cooled, and filtered. An excess of phospho-molybdic acid is added to the filtrate, and the pp. is washed with water containing nitric and phosphomolybdic acids. The still moist pp. is washed into a flask, made distinctly alkaline by the addition of barium hydrate, and distilled into a bulb apparatus charged with hydrochloric acid, which absorbs ammonia and the volatile bases. The residue in the flask, containing the non-volatile bases, is freed from barium hydrate by a current of carbon dioxide, evaporated to dryness, and the bases extracted by means of strong alcohol. The filtered alcoholic solution often yields on evaporation the alkaloids in a sufficient state of purity to admit of their being weighed, converted into hydrochlorides, and submitted to tests. Sometimes, however, they must be purified by re-solution and re-crystallisation from absolute alcohol, ether, chloroform, &c.

The method of Usлar and Erdmann (*A.* 120, 121) is not much employed in this country, the evaporation of amyl alcohol being a disagreeable operation; but it is nevertheless a valuable process for the separating of strychnine and morphine. It is practised as follows:—The suspected matter, if solid, is made into thin paste with water, slightly acidulated with hydrochloric acid, and digested at a temperature of 70° for an hour or two. It is then strained through a moist piece of cambric, and the solid residue on the cloth is well exhausted with hot very dilute hydrochloric acid. The combined liquids after filtration are made slightly alkaline with ammonia, mixed with clean sand, and evaporated to dryness on the water-bath. The residue from the evaporation is extracted three or four times with hot amyl alcohol and the mixed liquids are filtered. The filtrate is shaken violently in a stoppered tube with several times its volume of hot water acidulated with hydrochloric acid, which removes the alkaloids, leaving colouring matters and fat in the alcohol. The alcohol is pipetted off, and the hot acid solution is repeatedly washed by agitation with fresh portions of amyl alcohol until all fat and colouring matter is removed, after which the clear aqueous liquid is concentrated by evaporation, made alkaline with ammonia, and well shaken with fresh hot amyl alcohol four or five times. These alcoholic liquids are mixed, filtered through a filter moistened with amyl alcohol to remove water, and evaporated in a tared basin, when the alkaloids will be left in a sufficiently pure condition to be dissolved and tested, previous to which they should be weighed. Occasionally a coloured residue is obtained which requires re-solution in aqueous acid, agitation with amyl alcohol, alkalisation with ammonia, and re-extraction with amyl alcohol, in order to obtain the alkaloids in a sufficiently pure state for testing. With morphine the process, though tedious, works well.

Scheibler's process is based upon the precipitation of the alkaloids by phosphotungstic acid, a reagent prepared by treating sodium tungstate in solution with half its weight of phosphoric acid, when crystals of phosphotungstic acid slowly form. These are dissolved, and the process in detail is carried on in the same manner as Sonnenschein's phosphomolybdic acid process, substituting the phosphotungstic for the phosphomolybdic solution as a precipitant. It is sometimes recommended to precede the ppn. of the alkaloid by the addition of lead acetate to remove colouring matter, and then to remove the excess of lead by hydrogen sulphide; but some of the alkaloid present is apt to be removed with the lead pps. Nor should animal charcoal be used as a decolorant, as this is still more effective in withdrawing the alkaloids from solution. Indeed the obstinacy with which the alkaloids adhere to animal charcoal has been utilised by Graham, Hofmann, and Redwood as a means of

separating strychnine from beer and other liquids (*C. J.* 5, 173).

The following scheme serves for the detection of the more commonly occurring poisonous alkaloids. The alkaloids are brought into acid aqueous solution, and this is shaken with ether:—

I. *The ether withdraws from the acid aqueous solution*, and leaves on evaporation:

1. *Colchicine.*—Its solution is yellow, and is turned to a violet colour by strong nitric acid. Its solution in HClAq, when made alkaline with caustic soda, develops an orange-red colour.

2. *Digitalin.*—When dissolved in conc. H_2SO_4 and a minute quantity of bromine water is added, a reddish-violet tint is produced, which, on the addition of water changes to a green.

3. *Picrotoxin.*—Reduces Fehling's solution.

The solution is made alkaline with sodium bicarbonate, and again shaken with ether.

II. *Ether removes from the alkaline solution*, and leaves on evaporation:

1. *Nicotine.*—Oily droplets, having a tobacco-like odour. Its aqueous solution is not ppd. by chlorine water, nor does it become coloured when warmed. Warmed with hydrochloric acid the alkaloid becomes violet, and then on the addition of nitric acid orange-coloured.

2. *Coniine.*—Oily droplets having a mouse-like odour. Its aqueous solution is ppd. by chlorine water, and becomes coloured when warmed. Dry hydrochloric acid gas turns the alkaloid at first red, and then to a violet colour.

3. *Lobeline.*—Oily droplets yielding no very definite chemical reactions.

4. *Brucine.*—Turned rosy-red by strong sulphuric acid not quite free from oxides of nitrogen. The alkaloid is reddened by strong nitric acid, and the red solution changes to a bluish violet on the addition of a solution of stannous chloride.

5. *Strychnine.*—No coloration on the addition of strong H_2SO_4. On the further addition of solid potassium dichromate, MnO_2, or PbO_2, a violet-blue coloration is immediately produced, passing gradually into a cherry-red, the colour only slowly disappearing.

6. *Narcotine.*—It become first yellow, then bluish-violet when warmed with strong sulphuric acid. Its solution in strong H_2SO_4 becomes red on the addition of a trace of nitric acid. Sulphomolybdic acid turns the alkaloid green.

7. *Veratrine.*—With strong sulphuric acid it becomes yellow, orange, and finally cherry-red. Its solution in cold concentrated hydrochloric acid is colourless, but gradually changes to a deep red when boiled.

8. *Jervine.*—The salts of this alkaloid, except the acetate and phosphate are only very sparingly soluble in water and acid solutions. Its solution in acetic acid is ppd. by nitric acid and by potassium nitrate.

9. *Atropine.*—An odour of hawthorn is developed when the alkaloid, is warmed with strong sulphuric acid and potassium dichromate; and the solution becomes green from reduction of chromic acid. Evaporated to dryness with fuming nitric acid, and the residue touched with an alcoholic solution of potash, a fine purple colour is produced.

10. *Aconitine* can only be identified by its physiological properties. The chemical tests for pure aconitine are not characteristic.

11. *Gelsemine.*—With strong sulphuric acid and potassium dichromate, a reddish-purple or cherry-red colour is developed, quickly passing into bluish-green or blue.

12. *Physostigmine.*—Its solutions, whether acid or alkaline, become reddish on exposure, and this colour is discharged by sulphurous acid and the thiosulphates. Treated with sulphuric acid and bromine-water, it yields a brown-red colour.

III. *There remain in the alkaline aqueous solution*:—

Morphine, curarine, and cytisine. The first may be separated by shaking with acetic ether, and is identified by the usual tests—nitric acid, ferric chloride, iodic acid and starch, and sulphomolybdic acid. Curarine may be ppd. by phosphomolybdic acid after acidification with nitric acid. The pp. is decomposed by barium hydrate, and the alkaloid extracted by absolute alcohol (*v.* Sonnenschein's process, *ante*); it gives a reddish colour with sulphuric acid, and reacts somewhat like strychnine with sulphuric acid and potassium dichromate. Curarine, however, is not precipitated from its solutions by potassium dichromate.

Cytisine yields no definite chemical reactions.

The following are the chief trustworthy tests for the more commonly occurring poisonous alkaloids, &c.:—

Aconitine.—This alkaloid, as well as the closely allied alkaloids pseud-aconitine and japaconitine, when pure, yield no characteristic chemical reactions. The colour reactions with sulphuric and phosphoric acids that have been described by authors are untrustworthy, and due to impurities.

Apomorphine.—Its salts turn green on exposure to light and air, and its solutions on boiling. With sodium bicarbonate its solutions yield a pp. which turns green on standing, and forms with ether a purple, and with chloroform a violet, solution. Its solutions strike a red colour with ferric chloride and with nitric acid.

Atropine.—When warmed with strong sulphuric acid—or, more quickly, when evaporated to dryness with baryta-water, and the residue heated—an odour of stale hawthorn flowers is developed.

Brucine.—It is turned of a blood-red colour by nitric acid; and the red solution becomes violet on the cautious addition of a solution of stannous chloride. It yields an orange-red with sulphomolybdic acid; and with sulphuric acid and potassium dichromate a deep orange-red colour.

Caffeine.—Crystallises in silky needles. Evaporated to dryness with dilute hydrochloric acid and a fragment of potassium chlorate, a pink residue is left, which turns violet on the addition of ammonia.

Cinchonine.—It is difficult to get any characteristic reaction for this base. Its sulphate is soluble in chloroform, and is non-fluorescent—characters which distinguish it from quinine.

Cocaine.—Is not coloured by concentrated acids. When evaporated to dryness with alcoholic potash, the residue when warmed with

dilute sulphuric acid evolves an aromatic odour of benzoic acid.

Colchicine.—Nitric acid strikes a violet colour, which on the addition of sodium hydrate changes to a fine orange. Strong sulphuric acid dissolves the alkaloid to a greenish yellow colour, and on the addition of a drop of dilute nitric acid a play of colours, beginning with violet, is manifested. The subsequent addition of caustic soda yields a fine rose tint.

Coniine.—Oily, and of a mouse-like odour. Its dilute aqueous solution fumes with strong hydrochloric acid, and after acidification gives no pp. with bromine-water until supersaturated with sodium hydrate, when a white pp. forms.

Curarine.—Is turned blue violet when touched with sulphuric acid and potassium dichromate added; but the colour is more persistent than in the case of strychnine.

Cytisine.—This alkaloid is insoluble in ether, benzene, chloroform, and carbon disulphide. It dissolves in sulphuric acid without colour, but the subsequent addition of nitric acid produces an orange coloration. Nitric acid dissolves cytisine without colour, but on warming the mixture becomes orange-red.

Emetine is said to strike a blood-red colour with strong nitric acid, but the writer believes that this is due to impurities, and that tests for emetine are desiderata.

Gelsemine.—Sulphuric acid and potassium dichromate produce an immediate but evanescent violet coloration, and the chromate is quickly reduced. The alkaloid is naturally associated with gelsemic acid, a substance which in alkaline solution fluoresces strongly, and is yellow by transmitted, blue by reflected light.

Hyoscyamine.—No good chemical test for this alkaloid is known.

Jervine.—The salts of this alkaloid, especially the acetate, are ppd. by nitric acid and by potassium nitrate.

Morphine gives with nitric acid a deep red colour, not materially altered by the subsequent addition of stannous chloride. With sulphuric acid and potassium dichromate a green coloration is gradually developed. Ferric chloride gives a blue or blue-green coloration. It liberates iodine from iodic acid, and the mixture shaken with chloroform imparts a violet tint to this; but the brown colour is only deepened and altered in tint by ammonia. Sulphomolybdic acid gives an immediate purple coloration.

Narcotine.—Uncoloured by sulphuric acid, except this contains a trace of nitric acid, when a fine cherry-red colour is gradually developed, and is persistent. Its acidulated solution when warmed with bromine-water, added drop by drop, develops a purple or violet tint.

Nicotine.—Oily, and having the odour of tobacco. Freely soluble in water. Its acidulated solutions give a copious pp. with bromine-water, and this pp. disappears when excess of sodium hydrate is added.

Physostigmine.—Sulphuric acid gradually produces a reddish colour. Its solutions acquire a red colour on standing, and at once when treated with sodium hydrate and warmed, and on evaporation leave a bluish residue which on acidulation affords a dichroic (red and blue) solution, which becomes permanently red on standing.

Pilocarpine affords no very characteristic chemical reactions. With sulphuric acid and potassium dichromate a green colour, due to reduction, is developed.

Piperine has the pungent fragrant odour of pepper. It is turned of a deep red colour by sulphuric, and of an orange colour by nitric acid.

Quinine.—Its solution in sulphuric acid is fluorescent. Treated with bromine-water and then excess of ammonia added, an emerald green coloration is produced.

Salicin.—A neutral glucoside. It is not withdrawn from its acid or alkaline solutions by ether, benzene, or chloroform, and hence is not obtained in the ordinary processes for the separation of the alkaloids. It is turned of a cherry-red colour by sulphuric acid, and then on the addition of potassium dichromate an odour of meadow-sweet is evolved. Fused and partially sublimed in a test-tube, and then dissolved in water, ferric chloride strikes a violet colour.

Strychnine.—Sulphuric acid gives no colour till potassium dichromate, MnO_2, PbO_2, or ferricyanide of potassium is added, when immediately a fine blue-violet colour is produced which gradually passes into reddish-violet, red, and finally cherry-red. Evaporated to dryness with fuming nitric acid, and the residue moistened with alcoholic potash a deep orange colour is produced.

Veratrine.—Touched with strong sulphuric acid, this alkaloid gradually develops a fine red colour, or immediately on warming. Its solution in cold strong hydrochloric acid is colourless, but becomes intensely red on boiling.

T. S.

ALKAMINES, alcamines, alkines, or alcines. Names used by Ladenburg to denote substances that contain both alcoholic hydroxyl and amidogen, such as oxy-ethyl-amine, $C_2H_4(OH).NH_2$.

ALKANET. The commercial name of two different plants. True alkanet is *Lawsonia inermis*, false alkanet is *Anchusa tinctoria*. The leaves of *Lawsonia* contain a yellow dye, its roots contain a red pigment, used as a cosmetic. The root of *Anchusa* (*Orcannette, Radix Alcannæ spuriæ*) contains anchusin.

Anchusin or Alkannin $C_{35}H_{40}O_8$ (Bolley a. Wydler, *A.* 62, 141) or $C_{17}H_{20}O_4$ (Pelletier, *A.* 6, 27) or $C_{15}H_{14}O_4$ (Carnelutti a. Nasini, *G.* 1880, 283; *B.* 13, 1514). Obtained by extracting the root of *Anchusa tinctoria* with petroleum; the crude product is treated with dilute potash, the filtrate is shaken with ether, and the alkannin is ppd. by a current of CO_2. It is a brownish-red mass with a metallic lustre; sol. ether, chloroform, and acetic acid, sl. sol. alcohol. Softens below 100°. Alcoholic solutions give with baryta-water a blue pp. of a barium compound. NaOAc and Ac_2O produce a crystalline diacetyl derivative: $C_{15}H_{12}Ac_2O_4$(?). Nitric acid forms oxalic and succinic acids. Alkannin appears to be allied to santalin. An alcoholic solution of alkannin dyes cotton mordanted with alum, violet; iron mordants give a grey colour. Turned blue by alkalis, especially ammonia (Böttger, *J. pr.* 107, 46; Enz, *J.* 1870, 935). Alkannin, unlike rosaniline, is not abstracted by cubes of gelatin from its solution. Its absorption-spec-

trum shows 3 bands, dividing the spectrum between D and the blue strontium line into 4 equal parts. On adding ammonia the red solution turns blue, now showing 2 bands, one at D, the other in the red, two-thirds of the way towards the lithium line (A. Dupré, *C. J.* 37, 672).

ALKARSIN. Name given by Bunsen to cacodyl or arsenic di-methide (*q. v.*), C_2H_6As, as being empirically alcohol in which O has been displaced by As (*A.* 24, 271).

ALKYL. An alcohol radicle.

ALKOYL. An acid radicle.

ALLANIC ACID $C_4H_5N_5O_5Aq$.

Formed, together with urea and allanturic acid by the action of nitric acid in the cold on allantoïn (E. Mulder, *A.* 159, 353). Stellate needles (from water). Sl. sol. cold water. Decomposes at 210°–220° without melting. Does not give off gas with HNO_3 containing N_2O_4. Gives no pp. with $CaCl_2Aq$ and NH_3Aq. Gives pps. with $AgNO_3Aq$ and NH_3Aq, and with basic lead acetate, but not with neutral lead acetate.

Salts.—NH_4A': prisms.—$HO.Pb.A'$: ppd. by basic lead acetate.—$2PbA'_2 5Pb(OH)_2$—AgA' aq: amorphous pp.

ALLANTOÏC ACID

$C_4H_8N_4O_4$ *i.e.* $NH_2.CO.NH.CH(CO_2H).NH.CO.NH_2$

A solution of allantoïn in aqueous potash which has stood for some days, no longer gives a pp. with acetic acid, even after some time; but if a little alcohol be also added, and the liquid be left in an exsiccator over lime, crystalline potassic allantoate, KA', separates (E. Mulder, *A.* 159, 362; Schlieper, *A.* 67, 231; Ponomarew, *J. R.* 11, 13). The solution of potassic allantoate gives crystalline pps. with $Pb(OAc)_2$ and $AgNO_3$, but not with $BaCl_2$. $BaCl_2$ and alcohol give a hygroscopic curdy pp.

Salts.—NH_4A'—NaA' aq.—KA'.—BaA'_2 2aq.—PbA'_2 aq.—AgA'.

ALLANTOÏN $C_4H_6N_4O_3$ *i.e.*

$$CO\begin{cases}NH.CO\\ \quad\;\; |\\ NH.CH.NH.CO.NH_2\end{cases}$$

$$\text{or } CO\begin{cases}NH.CH(OH)\\ \quad\;\; |\\ NH.C{:}N.CO.NH_2\end{cases}$$

Mol. w. 158. S. ·62 at 20°; 3·3 at 100°.

Occurrence.—In the allantoïc liquid of the cow (Lassaigne, *A. Ch.* [2] 17, 301; compare Vauquelin, *A. Ch.* 33, 269). In urine of sucking calves (Wöhler, *A.* 70, 229). Occasionally in urine of dogs (Salkowski, *B.* 9, 721; 11, 500; Meissner a. Jolly, *Z.* 1865, 131). In the young leaf-buds of the plane and maple, and in the bark of the horse-chestnut tree (E. Schulze, *B.* 14, 1602; *J. pr.* 133, 147; *H.* 9, 425). In wheat, to the amount of ·5 p.c. of the embryo (Richardson a. Crampton, *B.* 19, 1181).

Formation.—1. By treating uric acid with boiling water and PbO_2 (Liebig a. Wöhler, *A.* 26, 244; E. Mulder, *A.* 159, 349), with KOH and potassic ferricyanide (Schlieper, *A.* 67, 216), or with $KMnO_4$ (Claus, *B.* 7, 227).—2. By heating glyoxylic acid (1 pt.) with urea (2 pts.) eight hours at 100° (Grimaux, *C. R.* 83, 62).—3. By the action of nitrous acid on dialuric acid (Gibbs, *A. Suppl.* 7, 337).—4. By heating mesoxalic acid with urea at 110° (Michael, *Am.* 5, 198).

Properties. — Glassy monoclinic prisms (Dauber, *A.* 71, 68). Tasteless. Neutral. Readily soluble in alcohol.

Reactions.—1. Dry *distillation* gives ammonic carbonate and cyanide, and charcoal.—2. Gently heated with *hydrochloric* or *nitric acid* it gives urea and allanturic acid.—3. Hot *sulphuric acid* forms CO_2, CO, and NH_3.—4. Boiled with *baryta-water*, CO_2, NH_3, oxalic acid, and hydantoïn are got (Baeyer, *A.* 130, 161).—5. Hot conc. *potash* forms CO_2, NH_3, oxalic acid, and acetic acid.—6. Cold *potash* slowly forms allantoïc acid (*q. v.*).—7. *Nitric acid* of S.G. 1·35 forms, on boiling, allanic acid (*q. v.*).—8. *Potassic ferricyanide* and KOH form allantoxanic acid (Mulder, *B.* 8, 1291).—9. *Sodium amalgam* forms glycoluril, $C_4H_6N_4O_2$ (Strecker a. Rheineck, *A.* 131, 119).—10. *Hydric iodide* reduces it to urea, and hydantoïn or glycolyl-urea (Baeyer, *A.* 117, 178).

Tests.—1. A conc. solution of furfurol, to which a little HCl has been added, gives a violet colour with an aqueous solution of allantoïn (Schiff, *B.* 10, 771).—2. Mercuric nitrate (but not chloride) gives a pp., as with urea. 100 g. of dry allantoïn require 172 g. of mercuric oxide. The pp. is $(C_4H_6N_4O_3)_4 5HgO$.

Compounds with Bases.—These are formed by boiling aqueous solutions of allantoïn with metallic oxides. They are sparingly soluble (Limpricht, *A.* 88, 94).—

$(C_4H_6N_4O_3)_2CdO$.—$C_4H_6N_4O_3ZnO$.—
$(C_4H_6N_4O_3)_8 5HgO$.—$(C_4H_6N_4O_3)_3 2HgO$.—
$(C_4H_6N_4O_3)_4 3PbO$.—$(C_4H_6N_4O_3)_6 CuO$.

The following are described as true salts: $AgC_4H_5N_4O_3$, got as a pp. by ammoniacal $AgNO_3$.—$KC_4H_5N_4O_3$: from allantoïn, KOHAq, and alcohol, in exsiccator.

Nitrate $C_4H_6N_4O_3HNO_3$. Amorphous. Decomposed by water or alcohol into HNO_3 and allantoïn.

Constitution.—The constitutional formulæ given above are chiefly based upon *Formation* 2 and *Reaction* 10.

ALLANTOXAÏDIN

$$C_3H_3N_3O_2 \text{ aq } i.e. \; CO\begin{cases}NH.CO\\ \quad\;\; |\\ NH.C{:}NH\end{cases} \text{aq.}$$

When allantoxanic acid is liberated from its salts, it at once splits up into CO_2 and this body (Ponomarew, *J. R.* 11, 47). Glittering prisms or tables. V. sol. boiling water, sl. sol. cold water or alcohol, insol. ether. Decomposed by heat, giving off HCN, HCNO, and NH_3. Acid reaction. Boiled with water, or treated with cold Na_2CO_3Aq, it splits up into formic acid and biuret.

Salts.—KA': ppd. by alcohol.—AgA'.

ALLANTOXANIC ACID $C_4H_3N_3O_4$ *i.e.*

$$CO\begin{cases}NH.CO\\ \quad\;\; |\\ NH.C{:}N.CO_2H\end{cases}$$

Formation.—1. Allantoïn dissolved in aqueous KOH is treated with potassic ferricyanide until the colour is permanent. Acetic acid is then added, when $C_4H_2KN_3O_4$ is ppd. (Van Embden, *A.* 167, 39).—2. From allantoïn, KOH, and $KMnO_4$ (Mulder, *B.* 8, 1292; Ponomarew, *J. R.* 11, 19).—3. From oxalyl-di-ureïde and aqueous potash (P. *B.* 18, 982).

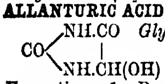
Properties.—The acid, liberated from its lead salt by H_2S, splits up into allantoxaïdin and CO_2.

Salts.—NH_4A': needles. —$(NH_4)_2C_4HN_3O_4$.

—KA′: silky needles. S. ·86. Boiled with water, it gives CO_2, biuret, and formic acid. Reduced by sodium-amalgam to hydroxonic acid.—$K_2C_4HN_3O_4$ aq: v. sol. water, insoluble in dry alcohol.—$Ba(C_4H_2N_3O_4)_2$ 6aq.—$BaC_4HN_3O_4$ 2aq.—$Pb(C_4H_2N_3O_4)_2$ 1½aq: very thin needles.—$PbC_4HN_3O_4$.—$AgC_4H_2N_3O_4$: crystalline pp.—$Ag_2C_4HN_3O_4$: gelatinous.

Ethyl ether $C_4H_2EtN_3O_4$: from AgA′ and EtI.

ALLANTURIC ACID $C_3H_4N_2O_3$ *i.e.*



Glyoxyl-urea.

Formation.—1. By boiling allantoïn with HNO_3, HCl or PbO_2 or heating with water at 140° (Pelouze, *A. Ch.* [3] 6, 71; Mulder, *A.* 159, 359).—2. Formed, together with glycoluril and urea, by action of sodium-amalgam on allantoïn (Reinecke, *A.* 134, 220).—3. By boiling allantoïc acid or alloxanic acid with water (Ponomarew, *J. R.* 11, 15; Schlieper, *A.* 56, 5).—4. By oxidation of hydantoïn (Baeyer, *A.* 117, 179; 130, 160).—5. By boiling uroxanic acid with water (Medicus, *B.* 9, 1162; Ponomarew, *B.* 11, 2155).

Properties.—A deliquescent gummy mass. Insol. alcohol. Boiling potash forms CO_2, NH_3, acetic acid, and oxalic acid (Medicus, *B.* 10, 544).

—Salts. These are amorphous.—KA′HA′ 2aq. S. 10.—BaA'_2 3aq.

ALLENE. Name sometimes used instead of ALLYLENE.

ALLITURIC ACID $C_6H_8N_4O_4$.

S. 5 or 6 at 100°. Obtained from an aqueous solution of alloxantin, mixed with HCl, by rapidly evaporating to a small bulk, and treating the resulting powder with HNO_3 which dissolves alloxantin but not alliturio acid. The latter crystallises from water as a bulky yellowish-white powder (Schlieper, *A.* 56, 20). Not attacked by conc. H_2SO_4 or HNO_3. Evolves NH_3 when boiled with KOH.

ALLO.—A prefix proposed by Michael (*B.* 19, 1378) to denote unexplained isomerism; thus fumaric acid would be called allo-maleic acid.

ALLOCAFFEÏNE $C_8H_9N_3O_5$.

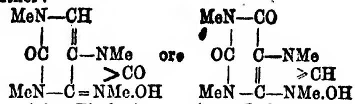
[196°]. (E. Fischer, *A.* 215, 276).

Formation.—1. Obtained by action of water on the unstable product of addition of bromine to caffeïne methylo-hydroxide.—2. One of the products of action of HCl and $KClO_3$ on caffeïne methylo-hydroxide (Schmidt a. Schilling, *A.* 228, 162).

Small white trimetric crystals, $a:b:c = \cdot6953:1:\cdot5401$, soluble in benzene, chloroform, and hot water, nearly insoluble in cold water, sparingly in alcohol or ether.

Reactions.—1. Decomposed by *boiling water* into CO_2 and methyl-caffuric acid. Allocaffeïne is therefore probably methyl-apocaffeïne.—2. HNO_3 (S.G. 1·2) gives cholestrophane, methylamine, and CO_2.—3. HCl and $KClO_3$ form dimethyl-alloxan, amalic acid, cholestrophane, methylamine, and CO_2.—4. *Bromine* appears to form an addition product, but it is decomposed by water into allocaffeïne, cholestrophane, and methylamine hydrobromide.—5. Boiling baryta forms sarcosine, formic acid, and CO_2.

Constitution.—Inasmuch as it splits off $NMeH_2$ in reactions where caffeïne splits off NH_3, the Me (and consequently OH also) must be attached to nitrogen, the formula being either:



(after Fischer) (after L. Medicus).

ALLOPHANIC ACID $C_2H_4N_2O_3$ *i.e.* $NH_2.CO.NH.CO_2H$ *Urea ν-carboxylic acid.* The free acid splits up at once into CO_2 and urea. Its ethers are formed by passing vapour of cyanic acid into alcohols: $2CONH + HOEt = NH_2.CO_2Et + CONH = NH_2.CO.NH.CO_2Et$. The ethers are sparingly soluble crystalline solids.

Salts.—BaA'_2: obtained from the ether by cold baryta-water (Liebig a. Wöhler, *A.* 59, 291). When boiled with water it gives off CO_2, deposits $BaCO_3$, and urea is left in solution. Dry distillation produces basic cyanate, NH_3, and CO_2. It gives no pp. with $AgNO_3$.—Salts of Ca, K, and Na have been prepared.

Methyl allophanate $NH_2.CO.NH.CO_2Me$ (Richardson, *A.* 23, 138).

Ethyl allophanate EtA′. [191°]. 1. From alcohol and the vapour of cyanic acid (L. a. W.). 2. From $ClCO_2Et$ and urea (Wilm a. Wischin, *Z.* [2] 4, 5).—3. Together with oxamide and alcohol by heating urea with oxalic ether at 135°–170° (Grabowski, *A.* 134, 115).—4. From potassic cyanate, alcohol, and chloro-acetic ether (Saytzeff, *A.* 135, 230) or chloroformic ether, $ClCO_2Et$ (Wilm, *A.* 192, 244).—5. From potassic cyanate, alcohol, and HCl (Amato, *G.* 3, 469). Small needles. Tasteless. Sl. sol. cold water, more soluble in alcohol. V. sl. sol. cold ether (difference from carbamic ether). At 190° it slowly changes to alcohol and cyanuric acid. Alcohol at 160° converts it into carbamic ether: $NH_2.CO.NH.CO_2Et + HOEt = 2NH_2CO_2Et$ (Hofmann, *B.* 4, 268).

Acetyl derivative, $NHAc.CO.NH.CO_2Et$. [107°]. Silky needles (from alcohol) (Seidel, *J. pr.* [2] 32, 273).

Benzoyl derivative $NHBz.CO.NH.CO_2Et$. [163°]. Together with alcohol, HCl, and CO_2 from benzoyl chloride and urethane (Kretschmar, *B.* 8, 104).

Propyl allophanate PrA′. [150°–160°]. (Cahours, *J.* 1874, 334).

Amyl allophanate $C_5H_{11}A'$. [162°]. From cyanic acid and amyl alcohol (Schlieper, *A.* 59, 23). From amyl alcohol and urea (Hofmann, *B.* 4, 267). Unctuous pearly scales (from water).

Oxethyl allophanate $HO.C_2H_4A'$. [160°]. From glycol and cyanic acid vapour. Shining laminæ (from alcohol) (Baeyer, *A.* 114, 160).

Di-oxy-propyl allophanate $C_3H_5(OH)_2A'$. [160°]. From glycerin and cyanic acid vapour (B.). Plates (from alcohol). Sol. water. Heated with baryta-water, it forms $BaCO_3$, urea, and glycerin.

Phenyl-allophanate PhA′. Cyanic acid vapour is passed into phenol; the product is dissolved in alcohol and ppd. by ether. Slender crystals. At 150° it splits up into cyanic acid and phenol (Tuttle, *J.* 1857, 451).

Propenyl-methoxy-phenyl-allophanate $C_{12}H_{14}N_2O_4$ *i.e.* $NH_2.CO.NH.CO.O.C_6H_3(C_3H_5).OCH_3$. From eugenol and cyanic acid vapour (Baeyer.

A. 114, 164). Needles. Insol. water. Sl. sol. cold alcohol.

Amide of allophanic acid
$NH_2.CO.NH.CO.NH_2$ v. BIURET.

ALLOTROPY (otherwise turned, otherwise formed, from ἄλλος = another, and τρόπος = manner) denotes the appearance of one and the same substance in several different states, distinguished from each other by different properties. The term was introduced by Berzelius in 1840 (*J.* No. 20 for 1839, pt. ii. p. 13), because he held the term 'isomerism' to be inadmissible where the subject of modification is an *elementary* substance, isomeric states being traceable to different modes of combining equal numbers of atoms of the same elements. In the view of Berzelius, accordingly, the allotropic modifications of *the elements* are not to be explained by differences in the arrangement of their atoms, but he expressed no opinion whatever about their actual cause. Since, however, he indicated it as probable that even in compounds the elements retain their allotropic states, and thereby often occasion isomeric forms of compounds (*J.* No. 23, p. 51; No. 24, p. 32), he appears to have been of opinion that the cause of the allotropic transformation is to be sought in a change in the atoms themselves. Now that we have learned to appreciate more correctly the doctrine of Avogadro, and so have become accustomed to consider the molecules of the majority of elements as particles composed, like those of compounds, of several atoms, the distinction introduced by Berzelius between allotropy and isomerism has lost its original meaning. But the term allotropy has been retained, being used, however, with reference not to elements only but also to compounds. Accordingly we distinguish between *allotropy of elements* and *allotropy of compounds*. The former, according to the modern use of the expression, embraces all the different forms in which an element appears; the latter only those cases in which, while the composition remains the same, there is a change in the physical, but none, or at any rate none of any consequence, in the chemical, properties, thus apparently warranting the assumption that there has been no change in the linkage of the atoms by which, doubtless, chemical behaviour is essentially determined. Allotropy of compounds is accordingly synonymous with physical, as opposed to chemical, isomerism. But since the two groups of properties are closely connected, and any change of the physical is usually accompanied by a change, however small, of the chemical also, no sharp line is to be drawn between the two kinds of isomerism.

On the other hand, the transformation of one allotropic form into another offers so many analogies to the transformation of one state of aggregation into another that, strictly speaking the three states of aggregation of any substance should be described as three allotropic modifications of it (Lehmann, *Z.K.* 1877. 1, 97). Hitherto, however, it has not been usual so to describe the states of aggregation, and, consequently, on this side also, the notion of allotropy is not to be defined with perfect exactness. The melting of ice, for example, is a transformation of the lighter into the heavier modification of water, for the particles of the lighter are still retained in the liquid state for some degrees above the melting point, and bring it about that the maximum of density appears not at 0° but at +4°. Something similar probably takes place in many, if not in all, other substances, only the difficulties of observation are greater. But as it has been observed that changes in the properties of a substance usually proceed differently and follow different laws according as the substance is near to, or more remote from, its melting-point (no matter whether above or below it), we may conclude that immediately below the melting point the solid substance already contains isolated portions of the liquid modification, and that above the melting point the liquid body still contains portions of the solid modification. But even if we do not account these changes of aggregation as instances of allotropy, the number of cases of allotropy as yet known, while suffering a very important diminution, will still remain pretty considerable.

I. ALLOTROPY OF THE ELEMENTS.—Allotropy, taken in the narrower sense, has hitherto been observed only in the non-metallic or semi-metallic elements. Among metals proper it has been found only as regards crystalline form, in which case it is usually known as *dimorphism* or *polymorphism*. Since, to the best of our present knowledge, the gaseous molecules of the metals consist of single atoms,[1] while those of the semi-metals and non-metals are composed of several atoms, the absence of allotropic modifications of the metals proper tells in favour of the present view, which is different from that of Berzelius, and is to the effect that allotropy of the elements, like isomerism of compounds, depends on differences in the mode of union of the atoms, and not on any changes in the atoms themselves. Polymorphism, occurring as it does even among metals, may be explained by supposing that there are differences in the arrangements of the atoms as well as of the molecules, while the existence of allotropic modifications in the melted, the dissolved, or the gasified, state points to differences in the constitution of the molecules, *i.e.* to different modes of uniting the atoms to form molecules.

The appearance of allotropy seems to be favoured by smallness of atomic weight, for not unfrequently in one and the same natural family allotropy shows itself only in the first members, while the members with higher atomic weights exhibit it either in some properties only or not at all. In the **family of the halogens**, F, Cl, Br, I, allotropy has not been observed, unless we consider as such the splitting of molecules at high temperatures into separate atoms (Victor Meyer). **Hydrogen** does not exhibit allotropy. On the other hand allotropy is found very notably in the first members of the **oxygen-sulphur family.** *Ozone* exhibits much more strongly marked chemical characters, and moreover a greater density, than oxygen. If the molecular weight of ordinary oxygen is represented by O_2, that of ozone is probably O_3, ozone being thus a polymeride of oxygen. *Sulphur* in each of its states of aggregation exhibits allotropic modifications, and these to some extent correspond with each other. In the solid state it is: (1) rhombic;

[1] It should not be forgotten that the data are most meagre.—ED.

D. = 2·07, melting-point 113° (Gernez), soluble in CS_2: (2) monoclinic; D. = 1·96, M.P. 117° (Gernez), soluble in CS_2: (3) amorphous plastic; D. = 1·90 to 1·93, insoluble in CS_2: (4) according to Gernez (*C. R.* 98, 144) and Sabatier (*C. R.* 100, 1346) crystallised in little rods with a lustre like that of mother-of-pearl. The last modification Maquenne (*C. R.* 100, 1499) considers to be distorted rhombic crystals, which according to Gernez are very easily produced out of the fourth modification (*C. R.* 100, 1584) without being identical with it. Liquid sulphur is: (1) immediately above the melting-point thin and clear: (2) at about 200° thick and dark: (3) at about 340° thin and dark. The vapour: (1) between the boiling-point (446°) and about 500° has V.D. = 6·6, molecular weight = S_6: (2) above 700° V.D. = 2·2, molecular weight = S_2. The behaviour of *selenion* is analogous to that of sulphur. When solid this substance is: (1) red, amorphous, vitreous, or pulverulent, D. = 4·26, soluble in CS_2: (2) red, crystallised, monoclinic, isomorphous with sulphur, D. = 4·51, soluble in CS_2: (3) gray, granularly crystalline, D. = 4·80, insoluble in CS_2. Whether the black foliated crystals, insoluble in CS_2, D. = 4·80, obtained from a solution of potassium selenide, are identical with the third modification remains to be determined. Liquid selenion is: (1) at low temperatures in a thin stratum light-red and transparent: (2) at higher temperatures, dark. Gaseous selenion under 1400° consists in part of molecules composed of more than two atoms: above 1400° all the molecules are diatomic, V.D. = 5·68, molecular weight Se_2. Of *tellurium* no allotropic form is known with certainty, yet it is worthy of remark that its electrical conductivity, like that of selenion, but contrary to that of all other conductors of the first class, increases with rising temperature. This may be explained by supposing the production of a modification with better conductivity. As regards the nitrogen family, the existence of any allotropic forms of *nitrogen* has not yet been conclusively proved, but solid *phosphorus* exists in three forms: (1) colourless, very easily burnt, soluble in CS_2 and in many oils, crystallising out of these solutions according to the regular system, D. = 1·83: (2) red, amorphous, D. = 2·18: (3) dark-red crystallised in rhombohedral forms, in the highest degree indifferent, D. = 2·34. The last two forms perhaps represent one and the same modification. In the liquid state there seems to be only one modification—the colourless; in the gaseous state, on the contrary, there appear to be two, since the vapour-pressure over colourless phosphorus is greater than that over red at the same temperature, and the vapour condenses under certain circumstances into the one modification and under other circumstances into the other. *Arsenic* is: (1) amorphous, D. = 4·72, less easily oxidised than the following variety: (2) crystallised in rhombohedral forms, D. = 5·73. Whether explosive *antimony* (Gore), D. = 5·83, is a distinct modification cannot be quite definitely determined, since it cannot be obtained free from chloride. For ordinary antimony D. = 6·71. Of *bismuth* no allotropic modification is known.

In the carbon family *carbon* exists: (1) as diamond, regular, very hard, D. = 3·52: (2) as graphite, either rhombohedral (Kenngott), or monoclinic (Clarke, Nordenskiöld), D. = 2·32: (3) amorphous charcoal, D. = 1·87 to 2·30, agreeing with graphite in many properties and hence perhaps not to be regarded as a distinct modification. *Silicon*: (1) amorphous, easily oxidised: (2) crystallised according to the regular system, D. = 2·20 to 2·49. The so-called graphitoidal variety consists of distorted regular crystals. Of *titanium* and *thorium* allotropic forms are not known. *Zirconium* has been obtained amorphous and crystallised. *Tin* also appears to be dimorphous.

The element boron is probably capable of allotropic modification, yet hitherto it has been obtained *pure* only in the amorphous form. The crystallised always contains aluminium or carbon. Some of the platinum metals, namely *iridium* and *palladium* are said to occur in two forms, regular and hexagonal.

II. Allotropy of Compounds, or Physical Isomerism, may be theoretically defined as *isomerism with identity of atomic linkage.* The following inorganic compounds exhibit remarkable instances of allotropy: *calcium carbonate* (as calc-spar and arragonite); *silica* (quartz, tridymite, agate); *titanium oxide* (rutile, brookite, anatase); the *nitrates of sodium, potassium, ammonium*, and *silver*; *sodium metaphosphate*; *arsenious* and *antimonious oxides*; the *sulphates* of *magnesium, iron*, and *copper*; *potassium dichromate*; *silver iodide*; *zinc chloride*; *mercuric chloride*; *manganous chloride*; and indeed many other substances. Many instances of allotropy have also been observed among the compounds of carbon, particularly in the following substances: *benzophenone*; *isohydrobenzoin diacetate* (Zincke); *dibromopropionic acid* (Tollens); *tolylphenyl ketone* (Van Dorp, Zincke); *metachloronitrobenzene*; *chlorodinitrobenzene* (1:3:4) (Laubenheimer); *oxycamphoronic acid* (Zepharowich); the benzoylated and anisylated *hydroxylamines* (Lossen); *hydroquinone*; *paranitrophenol*; *stilbene chloride*; *dibromofluorene* (Lehmann); *tetramethyldiamido-triphenyl-methane*; *diphenylnaphthylmethane*; *pentamethylleukaniline* (E. Fischer, Lehmann); *dibenzoyldiamidodibromodiphenyl* (E. Lellmann). No definite and regular relation between the composition of carbon compounds and the existence of allotropic forms of these compounds has as yet been recognised.

The production of allotropic modifications, and the transformation of one modification into another, are effected, as a general rule, by changes of temperature. The cases in which we are entirely ignorant of the conditions under which allotropic modifications are produced, are but few. The most notable is that of one of the modifications of carbon—the diamond, but on the other hand the transformation of diamond into graphite has been observed. One of the allotropic states usually corresponds to a specified interval of temperature, so that at a definite limit of temperature the one modification passes into the other. Yet we frequently succeed in cooling the modification belonging to the higher temperature below the lower limit, and sometimes also in heating the other modification above this limit, without any transformation taking place. But when such a modification is preserved above its fixed limit, the

state of equilibrium attained by its particles is unstable, and is often destroyed by very trifling causes, a particularly easy means of upsetting it being to bring the substance into contact with a crystal of the modification that is stable at the prevailing temperature. On transformation into the stable form thereupon ensuing, heat is produced or disappears, according as contraction or expansion takes place. This thermal effect may be very considerable.

The temperature of transformation has been determined for rhombic and monoclinic sulphur by L. Th. Reicher (*Z. K.* 1884. 8, 6) to be 95·6°. Below this the rhombic form is stable, above it the monoclinic, the other being unstable. The amorphous form is unstable at all temperatures below, and also for a considerable interval above, the melting point; the temperature at which it becomes stable has not been determined, but probably it lies not far below the boiling point. When cooled quickly both the monoclinic and the amorphous form may be kept a considerable time at comparatively low temperatures. One might be tempted to suppose that the modifications that have thus become unstable would pass into the stable forms the more easily the greater the distance of their temperature from that of transformation; yet below the temperature of transformation this is not the case; on the contrary, transformation into the rhombic modification ensues the more easily the higher the temperature and therefore the nearer it comes to the temperature of transformation. This is undoubtedly due to the circumstance that the mobility of the particles increases as the temperature increases. The behaviour of selenion is similar to that of sulphur. Amorphous selenion is produced only above the melting point, which is 217°, nevertheless when this variety is quickly cooled it remains stable for some time, and begins to pass into the grey crystalline form only at 80° (Hittorf); the progress of this change is however more rapid at 125°. The temperature of transformation of the red soluble crystals of selenion is about 110° (Mitscherlich).

The conditions under which phosphorus passes from one of its modifications into another are very remarkable. If colourless phosphorus is vaporised in a vessel too small to contain the whole of the phosphorus as vapour, the red variety is formed at 210° and upwards; the change proceeds more rapidly at 260°, and very quickly above 300°. Conversely, red phosphorus, if it can transform itself freely into vapour, and if the vapour is allowed to cool, is re-converted at 260° into the colourless form: the red modification is formed only if the vapour has been heated above a red heat and then allowed to cool (Hittorf). Arsenic vapour condenses below 220° to form amorphous arsenic; at a higher temperature to form crystallised. At 360° the former passes into the latter with production of heat. Tin is converted by very great cold, under conditions not yet exactly determined, into loosely cohering columnar aggregations of grey colour and diminished density (Fritsche, Petri, Schertel). Light too may bring about the production of allotropic modifications; through its influence selenion and tellurium temporarily acquire a better electric conductivity—a fact which has been applied in telegraphy. Phosphorus becomes red through the action of light. Electricity likewise may convert phosphorus, *in vacuo*, into the red modification, but perhaps the transformation may be due only to the heat produced.

Among compound substances the phenomenon of the transformation of one allotropic modification into another has been observed by many authors, but it has been studied with special attention by O. Lehmann (*passim*, and in later papers in *Z. K.*) He has proved that it obeys the same laws that hold for the elements. In most cases an unstable modification, differing from the ordinary stable one, is obtained by raising a substance to a high temperature and then cooling it quickly to a temperature a long way below that of transformation. It is supposed that in such circumstances the particles do not find time and opportunity to assume the position of equilibrium corresponding to the lower temperature. The unstable state thus produced may be assumed alike by solid, melted, and dissolved, substances, and may be maintained, especially at pretty low temperatures, for a long time. In many cases, *e.g.*, in that of hydroquinone, the one modification (in this case the unstable) is obtained by melting or subliming; the other form is obtained from solutions. In other cases, either form may be obtained from the same melted body, or from the same solution, according as it is brought into contact with a crystal of the one form or of the other. If fragments of crystals of both modifications are introduced simultaneously, both of them at first increase in size; but as soon as the two crystalline masses come into contact the form that is stable at the prevailing temperature grows into, and at the expense of, the unstable, while the latter dissolves or is consumed. As a general rule the modification that is unstable at a low temperature has a lower melting point than the stable, so that many substances on being heated are observed first to melt, then to solidify again, with transformation into the other modification, and finally to melt a second time. This phenomenon may be observed with special distinctness in the case of dibenzoyldiamidodibromodiphenyl, because here the melting points of the two forms lie unusually far apart. The needles of this substance crystallised out of alcohol melt at 195°, when quickly cooled the melted substance solidifies to a vitreous mass, which, when again heated, melts at 99°, re-solidifies in a crystalline form between 125° and 130°, and then melts once more at 195° (Lehmann).

Many compounds, especially inorganic compounds, behave like selenion; the form produced at high temperatures may remain stable far below the temperature of transformation, and may become unstable only on being heated to the neighbourhood of the temperature of transformation. Arragonite, the rhombic form of calcium carbonate, which separates from hot solutions (and according to G. Rose from very dilute cold solutions also) is perfectly stable at ordinary temperatures. If, however, a crystal is heated, it breaks up, long before giving off carbon dioxide, into a mass of small crystals of calc-spar (Haidinger), thus passing over into the rhombohedral form, which is produced at lower temperatures. Rock-crystal and amorphous

silica are perfectly stable at ordinary temperatures, but at the temperatures of the porcelain-kiln they are changed into tridymite, the third modification, which in turn is likewise stable at lower temperatures. As regards other substances, particularly organic compounds, the forms to be classed as unstable usually possess much less stability, but still of course they are not altogether destitute of it. This persistence in a state no longer completely stable may be explained by supposing that a certain impulse, or an increase of the proper motion of the particles, is required to change the state—to make the particles leave their respective positions and pass over into new ones. That the change is attained most easily and most surely by contact with a crystal of the stable modification, is undoubtedly due to the power of every crystal to give to the particles settling on it a definite and regular orientation and arrangement. L. M.

ALLOXAN $C_4H_2N_2O_4$ aq (and 4aq.)

i.e. $CO{<}{}^{NH.CO}_{NH.CO}{>}CO$. *Mesoxalyl-urea.* Mol. w. 142.—Discovered in 1817 by Brugnatelli, who named it erythric acid. Subsequently examined by Liebig a. Wöhler (*A.* 26, 256), and by Schlieper (*A.* 55, 253).

Formation.—1. By oxidation of uric acid by HNO_3 (S.G. 1·42) diluted with water (9 pts.) at 70°. By adding $SnCl_2$, alloxantin is ppd., and, after washing, is re-oxidised to alloxan by nitric acid (2 pts. of S.G. 1·52 mixed with 1 pt. of S.G. 1·42) in the cold (Liebig, *A.* 147, 366, *Bl.* [2] 9, 152).—2. From uric acid and aqueous Br, Cl, or I (M. E. Hardy, *Bl.* [2] 1, 445).—3. From xanthine, $KClO_3$, and HCl (E. Fischer, *A.* 215, 310).

Properties.—A warm saturated aqueous solution deposits on cooling trimetric efflorescent crystals (with 4aq). If the solution is kept warm while evaporating monoclinic prisms (with aq) are got. V. sol. water or alcohol, ppd. from solution by HNO_3. Astringent taste, reddens litmus, does not decompose $CaCO_3$. Aqueous solution turns the skin purple, imparting a peculiar smell.

Reactions.—1. Hot dilute *nitric acid* forms CO_2 and parabanic acid, the latter then becoming CO_2 and urea.—2. Boiling *potash* forms mesoxalic acid and urea.—3. Boiling very dilute *sulphuric acid* forms ammonic hydurilate.—4. Boiling aqueous HCl or H_2SO_4 forms alloxantin, which separates; dialuric acid, ammonic oxalate etc., remain in solution.—5. Boiled a long time with *water*, it forms CO_2, parabanic acid, and alloxantin.—6. By *reducing agents* (H_2S, $SnCl_2$, Zn and HCl) it is converted into alloxantin, and finally into dialuric acid.—7. Boiled with *ammonia and sulphurous acid*, it forms ammonic thionurate (*q. v.*).—8. KHO or *baryta* converts it into alloxanic acid; baryta or lime-water giving white pps. of baric or calcic alloxanate. If the alkali be in excess, the pp. contains mesoxalate. 9. Warm aqueous *ammonia* forms a yellow jelly of the ammonium salt of 'mycomelic acid' $C_4H_4N_4O_2$ (L. a. W.).—10. *Ferrous sulphate* gives a deep blue colour.—11. Boiled with water and PbO_2 there results CO_2, $PbCO_3$, and urea.—12. Boiling aqueous *lead acetate* forms lead mesoxalate and urea.—13. Boiling aqueous $NaNO_2$ and acetic acid form sodic oxalurate (Gibbs, *Am. S.* [2] 48, 215).—14. *Hydroxylamine hydrochloride* forms violuric acid.—15. With a dilute solution of *pyrrol* it forms crystalline pyrrol-alloxan (Ciamician a. Silber, *B.* 19, 106, 1708).—16. PCl_5 mixed with $POCl_3$ at 130° forms tetra-chloro-pyrimidine (Ciamician a. Magnaghi, *B.* 18, 3444).

Metallic derivatives. — $C_4Ag_2N_2O_4$.— $C_4H_2N_2O_4HgO$ 7aq: ppd. by mercuric nitrate.—

Compounds with Bisulphites.— $C_4H_2N_2O_4NaHSO_3 1\frac{1}{2}aq$: large crystals, v. sol. water.—$C_4H_2N_2O_4KHSO_3$ aq: m. sol. cold water, v. sol. hot water.—$C_4H_2N_2O_4NH_4HSO_3$ (Limpricht a. Wuth, *A.* 108, 41).

ALLOXANIC ACID $C_4H_4N_2O_5$

i.e. $NH_2.CO.NH.CO.CO.CO_2H$. *Mesoxaloxyl-urea.* S. (alcohol) about 20. (Liebig a. Wöhler, *A.* 26, 292; Schlieper, *A.* 55, 263; 56, 1; Städeler, *A.* 97, 122; Baeyer, *A.* 119, 126; 130, 159). Formed from alloxan by treatment with aqueous fixed alkalis or alkaline carbonates. White needles or warty masses. V. sol. water; sl. sol. ether.

Reactions.—1. *Boiling* the aqueous solution produces CO_2, leucoturic acid (*q. v.*), allanturic acid and hydantoïn.—2. Alloxanates are converted by *boiling water* into mesoxalates and urea.—3. *Nitric acid* forms CO_2 and parabanic acid.—4. HI reduces it to hydantoïn, giving off CO_2 (Baeyer).

Salts. The alkaline alloxanates are soluble in water. The normal salts of other metals are usually insoluble. Ferrous sulphate gives a dark blue pp. with potassic alloxanate. $NH_4C_4H_3N_2O_5$. S. about 30.—$BaH_2A''_2$2aq.— BaA''4aq. — $CaH_2A''_2$6aq. S. 5.—CaA''5aq. — CuA''4aq. S. 17 to 20. — $CuA''Cu(OH)_2$. — $PbH_2A''_2$2aq. — $Pb_3H_2A''_4$7aq. — PbA''aq. — $Pb_3A''_2(OH)_2$.—MgA''5aq.—NiA''2aq.— KHA''.— K_2A''3aq. — Ag_2A''.—SrA''4aq.—$ZnH_2A''_2$4aq.— $Zn_3OA''_2$8aq.

Iso-alloxanic acid $C_4H_4N_2O_5$. Obtained by the action of alkalis upon the red substance got by heating alloxan at 260° (L. Hardy, *A. Ch.* [4] 2, 372). A similar body may be got by the action of bromine-water on uric acid (Magnier de la Source, *Bl.* [2] 22, 56). Its solution then gives with baryta-water a splendid violet pp. of baric iso-alloxanate, which, however, when exposed to moist air soon changes to colourless baric alloxanate.

Salts.—$(NH_4)_2A''$: red powder: v. sol. water forming a purple solution, which gives with $AgNO_3$ an indigo blue pp., and with K_2CO_3 a violet colour.

ALLOXANTIN $C_8H_4N_4O_7$ 3aq.

(Liebig a. Wöhler, *A.* 26, 262; Fritzsche, *J. pr.* 14, 237).

Formation.—1. By action of warm dilute HNO_3 on uric acid.—2. By action of electrolysis or of reducing agents on alloxan (*q. v.*).—3. By dissolving alloxan in a concentrated aqueous solution of dialuric acid: $C_4H_2N_2O_4 + C_4H_4N_2O_4 = C_8H_4N_4O_7 + H_2O$.—4. By heating uranil or ammonium thionurate with dilute H_2SO_4.—5. By action of air on dialuric acid.—6. In the decomposition of caffeïne by chlorine.—7. By heating a mixture of malonic acid and urea with excess of $POCl_3$ (Grimaux, *C. R.* 87, 752; 88, 85).—8. By the prolonged action of H_2S upon di-bromo-barbituric acid (G.).

Properties.—Small oblique rhombic prisms.

Reddens litmus. V. sl. sol. cold water. Gives with baryta-water a violet pp. Reduces $AgNO_3$.

Reactions.—1. At 170° gives hydurilic acid, oxalic acid, CO_2, CO, and NH_3.—2. *Oxidation* gives alloxan.—3. *Reduction* forms dialuric acid.—4. *Ammonia gas* turns it red, forming murexide.—5. *Aqueous ammonia* forms a purple solution, long boiling bleaches it, uranil being formed. This is then converted into murexide by atmospheric oxidation.—6. The purple pp. produced by *baryta-water* disappears on boiling, baric alloxanate and dialurate being formed.

ALLOYS.—The word *alloy* was originally employed to designate the product obtained by mixing gold or silver with other metals; its application is now general, all mixtures or compounds of metals with each other being named alloys, except those containing mercury, which are termed 'amalgams.' For a detailed description of special alloys, reference must be made to one of the constituent metals; only the general properties of the alloys will be here considered.

On melting two metals together, or on melting one and adding the other, complete assimilation takes place in some cases and not in others. Thus, silver easily mixes or alloys with gold, copper, or lead; but neither silver nor copper can be readily induced to unite with iron. In the cases of those metals which do not completely mix when melted together it usually happens that a small quantity of one is taken up by the other; thus, Faraday and Stodart found that iron is able to absorb $\frac{1}{500}$th of its weight of silver with production of a homogeneous alloy, the properties of which are considerably different from those of iron; but that if more silver than $\frac{1}{500}$th of the mass of the iron is present, the greater part of the silver separates during cooling, and that which remains can be detected by the microscope. If silver is melted with addition of a small quantity of iron, the latter metal alloys to some extent; but it is impossible to obtain mixtures of these metals in any desired proportion. On the other hand, silver and copper, or silver and gold, form alloys in which the proportion of the two metals may be varied at will.

The physical properties of alloys are in some cases nearly the mean of those of their constituent metals; but in other cases a wide difference is observable between the properties of the alloy and the properties of the metals which have been used to form it. Matthiessen, to whom we owe most of our knowledge of the properties of alloys, divides all metals into two classes: (1) those which impart to an alloy their own physical properties, to a less or greater degree, according to the proportion in which they themselves exist in the alloy; and (2) those which do not come under class (1). To the first class belong the metals lead, tin, zinc, and cadmium; and to the second, in all probability, the other metals. The alloys themselves may also be divided into three groups: (*a*) those made of the metals belonging to class (1), (*b*) those made of metals of class (1) with class (2); and (*c*) those made of class (2) with one another. This classification is largely based on the relative conductivity for electricity of the metals and of the alloys which they form with each other. Matthiessen found that the metals placed in class (1), when alloyed with each other, give products the conducting powers of which for heat and for electricity are proportional to the relative quantities by volume of the constituent metals; but that this is not the case with alloys of the metals of class (1) with those of class (2), nor with the alloys of metals of class (2) with each other. As regards conductivity for heat and for electricity, Wiedemann and Franz have added to our knowledge by showing that the conducting powers of metals and their alloys for heat vary in a similar manner to that in which their conductivity for electricity varies. This statement has been confirmed and amplified by Sundall.

Matthiessen regards alloys of the metals of class (1) as solidified solutions of one metal in the other; but supposes that metals of class (2) enter into alloys in an allotropic form; and he further supposes that when metals are alloyed together one or more of the metals may undergo allotropic change. Thus, he regards as solidified solutions of the metals, alloys of lead with tin, cadmium with tin, zinc with tin, cadmium with lead, zinc with cadmium, and zinc with lead. He supposes that in the alloys of lead or tin with bismuth, tin or zinc with copper or with silver, one metal is dissolved in an allotropic modification of the other; and that in alloys of bismuth with gold or silver, palladium or platinum with silver, or of gold with copper or silver, both metals exist in allotropic forms. Matthiessen does not, however, ignore the fact that certain alloys contain their constituent metals in simple atomic proportions; for example, the alloys whose composition may be expressed by the formulæ $AuSn_5$, $AuSn_2$, and AuSn; but he regards alloys of intermediate composition as solidified solutions of such definite compounds in each other. It is known that zinc will not alloy with more than 1·2 p.c. of lead, nor will lead alloy with more than 1·6 p.c. of zinc; yet, by stirring, it is possible to obtain mechanical mixtures of such alloys with excess of one or other metal. Such mixtures are placed by Matthiessen in a class by themselves. Most of the alloys of silver and copper with each other are regarded by him as mixtures of various solidified solutions. The hypothesis of the existence in an alloy of one of the constituent metals in an allotropic form has received a certain degree of confirmation from experiments by Deville and Debray, who have observed that the iridium separated by the action of an acid on an alloy of that metal with zinc explodes when heated to 300°, and is changed by the explosion into ordinary iridium. Wiedemann has suggested that the contraction of alloys after solidification, which sometimes goes on for days, is due to the gradual occurrence of an allotropic change in the constituent metals, one modification being stable at high, and the other at low, temperatures. If the hypothesis of the occurrence of allotropic change during the formation of certain alloys is tenable, it is remarkable that such allotropic modifications of metals should be producible by pressure; for Spring has succeeded in producing Wood's alloy (containing bismuth, cadmium, and tin), and also brass, but the latter only partially, by exposing mixtures of the metals in fine powder to very high pressures.

On the whole, there appears to be a marked analogy between alloys and solutions. It is well known that the conductivity of water for electricity is nearly nil, but becomes considerable when the minutest trace of any salt is dissolved in it. Similarly, the conductivity of copper is greatly diminished by the admixture with it of minute quantities of other metals. Moreover, in many other cases a great modification is produced in the tenacity, malleability, &c., of metals by very small additions of foreign substances; as, for example, by the addition of small quantities of carbon, silicon, sulphur, or phosphorus, to iron, of phosphorus to copper, or of magnesium to nickel. And just as an aqueous solution of a salt must be heated to a temperature higher than that of the boiling-point of water before the whole of the water is removed, so it has been found that alloys of zinc, sodium, mercury, &c., must be heated to temperatures above those at which these metals volatilise before the metals in question are entirely removed from the alloys. The analogy between alloys and solutions has been strikingly shown by Guthrie. This physicist has found that that alloy of two metals which has the lowest melting-point does not contain the metals in atomic proportion, but is strikingly similar to an 'alloy' of two salts, such as that of nitrate of potassium and nitrate of lead. Alloys were obtained by him of bismuth and zinc (Bi = 92·85 p.c. Zn = 7·15 p.c.), melting at 248°; of bismuth and tin (Bi = 46·1 p.c. Sn = 53·9 p.c.), melting at 133°; of bismuth and lead (Bi = 55·58 p.c. Pb = 44·42 p.c.), melting at 122·7°; and of bismuth and cadmium (Bi = 59·19 p.c. Cd = 40·81 p.c.), melting at 144°. None of these alloys contains the metals in the proportion of their atomic weights, and the melting-point of each alloy is the lowest of all possible alloys of the specified pair of metals. Such alloys are termed by Guthrie *eutectic* alloys; they appear to be in some sense solidified solutions, resembling cryohydrates. We are still ignorant of the true nature of such mixtures, if mixtures they be.

Spring (*B.* 15, 595) has prepared several alloys by subjecting mixtures of the constituent metals to pressures of about 7,000 atmos. In this way he obtained brass, Wood's alloy (Bi, Cd, and Sn), and Rose's alloy (Bi, Pb, and Sn).

References.—Matthiessen, *B. A.* 1863, 37; and *C. J. Trans.* 1867, 201; also *P. R. I.* March 20th, 1868. Deville and Debray, *C. R.* 94, 1557. Spring, *B.* 15, 595. Wiedemann, *W.* 3, 237–250. Crookewit, *A.* 68, 290. Fürstenbach, *Bayerisches Industrie- und Gewerbeblatt*, 1869. Sundall, *A. Ch.* 119, 144. Crace-Calvert a. Johnson, *A. Ch.* 45, 454. Guthrie, *P. M.* June, 1884.

W. R.

ALLURANIC ACID $C_5H_4N_4O_4$ (?). Formed by evaporating an aqueous solution of equivalent quantities of urea and alloxan (Mulder, *B.* 6, 1012). Crystals; sl. sol. water. AgA′2aq.

ALLYL.—The radicle $CH_2{:}CH.CH_2$ is called Allyl, the isomeric radicle $CH_3.CH{:}CH$ being termed Propenyl.

DI-ALLYL C_6H_{10} *i.e.* $CH_2{:}CH.CH_2.CH_2.CH{:}CH_2$. *Hexinene.* Mol. w. 82. (59·3°) at 769 mm. (R. Schiff, *A.* 220, 91); (59·5°) (Zander, *A.* 214, 148). S.G. $\frac{11\cdot9}{4}$ ·6983; $\frac{0}{}$ ·7074 (Z.); $\frac{20}{4}$ ·688 (Brühl). C.E. (0°–10°) ·00138; (11·9°–59·3°) ·00156. S.V. 125·8 (S.); 125·7 (Z.). V.D. 2·84 (for 2·84). H.F.p. − 9260. H.F.v. − 11580 (Thomsen). μ_β 1·4079. R_∞ 45·99 (B.). *Critical temperature* 234·4°.

Formation.—1. From allyl iodide and Na (Berthelot a. de Luca, *A.* 100, 361), an alloy of sodium and tin (Würtz a. Leclanché, *A. Ch.* [4] 3, 155), or iron (Linnemann, *Bl.* [2] 7, 424).—2. By heating mercury allyl iodide, $IHgC_3H_5$, alone (Linnemann, *A.* 140, 180) or with aqueous KCy (Oppenheim, *B.* 4, 672).

Reactions.—1. Oxidised by *chromic acid mixture* gives carbonic and acetic acids.—2. Oxidised by $KMnO_4$ in neutral solution gives CO_2, acetic, oxalic, and succinic acids.—3. Oxidised by $KMnO_4$ in acid solution gives CO_2, acetic acid, and succinic acid (E. Sorokin, *J. pr.* 131, 1).

Constitution.—The formation of acetic acid by oxidation of di-allyl seems to favour the formula $CH_3.CH{:}CH.CH{:}CH.CH_3$; while the formation of succinic acid is more in accordance with the formula $CH_2{:}CH.CH_2.CH_2.CH{:}CH_2$, a formula that is further supported by the conversion of di-allyl into di-propargyl. The oxalic acid may be supposed to be formed by oxidation of the succinic acid. Acetic acid may be considered to be formed from intermediate hydrates,

$CH_3.CH(OH).CH_2.CH_2.CH{:}CH_2$

and $CH_3.CH(OH).CH_2.CH_2.CH(OH).CH_3$.

These bodies do, in fact, yield acetic acid when oxidised. According to Sabaneeff (*J. R.* 1885, 35) di-allyl forms two tetrabromides and must therefore be a mixture of two hydrocarbons.

Combinations.—1. When gaseous HI is passed into strongly cooled di-allyl, combination takes place, the product $CH_3.CHI.CH_2.CH_2.CHI.CH_3$ being formed, *v.* IODO-HEXANES.—2. A smaller quantity of HI forms the mono-hydro-iodide, $C_6H_{10}HI$, (165°), also formed from preceding by alcoholic KOH (*v.* IODO-HEXYLENE).—3. Similarly, fuming HCl forms two hydrochlorides.—4. HOCl forms $C_6H_{10}(HOCl)_2$, di-chloro-di-oxy-hexane (*q. v.*).—5. Br forms tetra-bromo-hexane.

ALLYL ACETATE $C_5H_8O_2$ *i.e.* $C_3H_5C_2H_3O_2$. Mol. w. 100. (103°–103·5°) at 735 mm. (R. Schiff, *A.* 220, 109), S.G. $\frac{20}{4}$ ·9276 (Brühl). S.V. 121·37 (S.). μ_β 1·4106. R_∞ 42·21 (B.).

ALLYL-ACETIC ACID

$C_5H_8O_2$ *i.e.* $CH_2{:}CH.CH_2.CH_2.CO_2H$. *Pentenoic acid.* (185°–188° cor.). S.G. $\frac{12}{12}$ ·9866; $\frac{15}{15}$ ·9842; $\frac{25}{25}$ ·9767. M.M. 6·426 at 14° (Perkin, *C. J.* 49, 211). Prepared by heating allyl-malonic acid (Conrad a. Bischoff, *B.* 13, 598) or from allyl-aceto-acetic ether (Zeidler, *B.* 8, 1035). Combines with Br_2 or HBr. Not reduced by *sodium-amalgam.* Oxidised by chromic acid to succinic and formic acids.

Salts.—KA′: scales; v. sol. water; solution not ppd. by Fe_2Cl_6.—CaA′$_2$ 2aq.: laminæ.—BaA′$_2$ 2aq.—AgA′ (Messerschmidt, *A.* 208, 92).

Ether.—EtA′: (142°–144°).

DI-ALLYL-ACETIC ACID $C_8H_{12}O_2$ *i.e.* $(C_3H_5)_2CH.CO_2H$. *Octinoic acid.* (220°) (C. a. B.); (218°–222°) (H.); (224°–226°) (R.); (227° cor.). S.G. $\frac{12}{12}$ ·9576; $\frac{15}{15}$ ·9555; $\frac{25}{25}$ ·9491. M.M. 10·344 at 16·4° (Perkin, *C. J.* 49, 212).

Formation.—From di-allyl-aceto-acetic ether (Wolff, *A.* 201, 49; Reboul, *Bl.* [2] 29, 228) or from di-allyl-malonic acid (Conrad a. Bischoff,

B. 13, 598). From iodo-di-allyl-acetic acid (*q. v.*) by reduction (Schatzky, *J. R.* 17, 79).

Properties. — Oil, of disagreeable odour. Insol. water. Volatile with steam.

Reactions.—1. Conc. HBr forms, probably, an addition product $(CH_3.CHBr.CH_2)_2CH.CO_2H$ which instantly splits off HBr forming

$$CH_3.CHBr.CH_2.CH\left\langle\begin{array}{l}CH_2.CH.CH_3\\ \qquad\quad |\\ CO.O\end{array}\right.$$

v. Bromo-oxy-octoic acid (Hjelt, *A.* 216, 73).—2. Br in $CHCl_3$ forms, probably, an addition compound, $(CH_2Br.CHBr.CH_2)_2CH.CO_2H$, but this instantly splits up into HBr and a lactone

$$CH_2Br.CHBr.CH_2.CH\left\langle\begin{array}{l}CH_2.CH.CH_2Br\\ \qquad\quad |\\ CO.O\end{array}\right.$$

v. Tri-bromo-oxy-octoic acid.

—3. HNO_3 (S.G 1·3) forms tri-carballylic acid (W.).

Salts.—$CaA'_2 2aq$: leaflets.– AgA'. S. ·41 at 15°. Ether.—EtA' (195°) (R.).

ALLYL-ACETO-ACETIC ETHER *v.* pp. 23, 25.

ALLYL-ACETONE

$C_6H_{10}O$ *i.e.* $CH_2:CH.CH_2.CH_2.CO.CH_3$

Methyl butenyl ketone. (129°). S.G. $\frac{27}{17.5}$ ·834. From allyl-aceto-acetic ether (Zeidler, *A.* 187, 35). Unpleasant smell. Forms with $NaHSO_3$ an amorphous compound, $C_6H_{10}O\,2NaHSO_3$ (O. Hofmann, *A.* 201, 81). Reduced by sodium-amalgam to hexenyl alcohol (*q. v.*).

DI-ALLYL-ACETONE

$C_9H_{14}O$ *i.e.* $(C_3H_5)_2CH.CO.CH_3$. (175°).

From di-allyl-aceto-acetic ether (Wolff, *A.* 201, 47).

ALLYL-ACETOPHENONE *v.* Phenyl butenyl ketone.

ALLYL-ACETOXIM

$C_6H_{11}ON$ *i.e.* $C_3H_5.CH_2.C(N.OH).CH_3$ (188° corr.). Formed by the action of hydroxylamine on allyl-acetone. Liquid. Soluble in alcohol, ether, benzene, CS_2, ligroine, acids, and alkalis. By aqueous acids it is resolved into its constituents. It combines with bromine to form a di-bromide (Nageli, *B.* 16, 496).

ALLYL ALCOHOL

C_3H_6O *i.e.* $CH_2:CH.CH_2OH$. [-50°]. (96·6°). S.G. $\frac{0}{0}$ ·8706; $\frac{15}{15.5}$ ·8576. S.V. 74·19. C.E. (0°-20°) ·00104 (Thorpe, *C. J.* 37, 208). S.H. ·6569 (Reis, *P.* [2] 13, 447). H.F.p. 31,200. H.F.v. 29,750. R∞ 27·09 (Brühl, *A.* 200, 175).

Occurrence.—Crude wood spirit contains not more than one-fifth per cent. (Aronheim, *B.* 7, 1381; Grodzki a. Krämer, *B.* 7, 1492).

Formation. — 1. Dry gaseous ammonia is passed into oxalate of allyl till a solid mass of oxamide, saturated with allyl alcohol, is obtained. The latter is then distilled off (Zinin, *A.* 96, 362).—2. Produced, together with isopropyl alcohol and acropinacone (*q. v.*), when acroleïn is treated with zinc and hydrochloric acid (Linnemann, *A. Suppl.* 3, 257).—3. By the action of sodium on dichlorhydrin (Hübner a. Müller, *Z.* 6, 344). — 4. The two atoms of chlorine may also be removed from dichlorhydrin by sodium-amalgam (Lourenço, *A. Ch.* [3] 67, 323), or by copper and potassic iodide (Swarts, *Z.* 1868, 259).—5. Allyl iodide (1 pt.) is heated with water (20 pts.) for 60 hours in a soda-water bottle at 100°. The yield is excellent (Niederist, *A.* 196, 350).

Preparation.—Glycerine (400 pts.) is slowly distilled with crystallised oxalic acid (100 pts.) and a little ammonic chloride (1 pt.), to convert any potassic oxalate into chloride. The receiver is changed at 190°, and the distillation continued up to 260°. The distillate, containing aqueous allyl alcohol, allyl formate, acroleïn, and glycerin, is rectified, dried, first with K_2CO_3, then over solid potash, and distilled. It then boils at 90°, but when the last traces of water are removed by quicklime, it boils at 96°. The yield is one-fifth of the weight of oxalic acid used (Tollens a. Henninger, *Bl.* [2] 9, 394; Brühl, *A.* 200, 174; Linnemann, *B.* 7, 854).

Theory of the Process. — Carbonic acid is first evolved freely (at 130°), but formic acid which must be produced at the same time ($H_2C_2O_4 = CO_2 + H_2CO_2$) reacts upon glycerin, producing monoformin: $C_3H_5(OH)_3 + H_2CO_2 = H_2O + C_3H_5(OH)_2(OCHO)$. The monoformin can be extracted with ether, and boils about 165° *in vacuo.* When distilled, monoformin splits up into allyl alcohol and carbonic acid:

$$C_3H_5(OH)_2(OCHO) = CO_2 + H_2O + C_3H_5(OH)$$

(Tollens, *A.* 156, 140). When a large quantity of oxalic acid is used, the excess of formic acid does not produce diformin, but comes off as formic acid (*q. v.*).

Properties. —A pungent liquid, with a burning taste. It mixes with water, alcohol, and ether.

Constitution.—That allyl alcohol has the formula $CH_2:CH.CH_2OH$ and not $CH_3.CH:CH.OH$ may be inferred from the fact that it yields no acetic acid when oxidised by nitric acid. A similar remark applies to allyl iodide (Kekulé a. Rinne, *B.* 6, 386).

Reactions.—1. *Chromic acid* oxidises it to CO_2 and formic acid; no acrylic acid is formed, but a pungent odour, which may be due to acroleïn, is observed (Hofmann a. Cahours, *A.* 100, 257; Rinne a. Tollens, *A.* 159, 110).—2. When allyl alcohol is heated, with inverted condenser, for 5 hours in a water-bath with *zinc* and dilute H_2SO_4, about 16 p.c. is reduced to *n*-propyl alcohol: $CH_2:CH.CH_2OH + H_2 = CH_3.CH_2.CH_2OH$ (Linnemann, *B.* 7, 862).—3. Solid *potash* at 100°-150°, in a flask with inverted condenser, forms *n*-propyl alcohol (by reduction), formic acid (by oxidation), ethyl alcohol, hydrogen, and other products (Tollens, *A.* 159, 92).—4. *Potassium* displaces hydrogen, forming gelatinous potassic allylate.—5. H_2SO_4 forms $(C_3H_5)HSO_4$.—6. Dilute H_2SO_4 or HCl at 100° forms an aldehyde, $C_6H_{10}O$ (c. 137°) (Solonina, *J. R.* 1885, i. 145).

Combinations.—1. With *chlorine* it forms *u*-dichlorhydrin $CH_2Cl.CHCl.CH_2OH$ (*q. v.*)—2. With *bromine* it forms a dibromide, called also dibromhydrin, $CH_2Br.CHBr.CH_2OH$, (214°). 60 grms. Br are dissolved in 300 grms. CS_2 and dropped slowly (in 4 hours) into a solution of 20 grms. of allyl alcohol in 100 grms. of CS_2. The product is distilled in vacuo (Michael a. Norton, *Am.* 2, 16; compare Kekulé, *A. Suppl.* 1, 138; Markownikoff, *J.* 1864, 490). Linnemann says there are two bromides (*B.* 7, 859).—3. When *iodine* is added to a solution of allyl alcohol in $CHCl_3$, it combines, and on evapora-

tion $CH_2I.CHI.CH_2OH$ separates as needles. Dilute Na_2CO_3 converts this into iodallyl alcohol [160°] (Hübner a. Lellmann, *B.* 14, 207).—4. ICl unites, forming $C_3H_5ICl(OH)$ (Henry, *B.* 3, 351).—5. With *cyanogen* it unites, forming $C_3H_5(CN)_2(OH)$, (151°) (Tollens, *B.* 5, 1045).—6. BaO combines, forming $BaO,2C_3H_6O$.—7. HClO unites, forming a little chlorhydrin (*q. v.*).—8. *Chloral* combines with allyl alcohol; the compound, $CCl_3.CH(OH)(OC_3H_5)$ [20·5°], (116°), is analogous to chloral alcoholate (Oglialoro, *G.* 4, 463).

DI-ALLYL-*p*-AMIDO-BENZOIC ACID $C_{13}H_{15}NO_2$ *i.e.* $(C_3H_5)_2N.C_6H_4.CO_2H$ [127°]. From allyl iodide and potassic *p*-amido-benzoate (Michael a. Wing, *Am.* 7, 198).

Di-allyl-*m*-amido-benzoic acid [90°] (Griess, *B.* 5, 1041).—HA'HCl aq.

DI-ALLYL-AMIDO-ETHYL ALCOHOL *v.* OXYETHYL-DI-ALLYLAMINE.

ALLYLAMINE C_3H_7N *i.e.* $CH_2:CH.CH_2.NH_2$ Mol. w. 57. (56°) (R. Schiff, *B.* 19, 565); (58°) (Oeser, *A.* 134, 7). S.G. $\frac{15}{}$ ·864 (O.) S.V. 78·38 (S.). H.F.p. −1140. H.F.v. −2880.

Formation.—1. From allyl cyanate (Cahours a. Hofmann, *A.* 102, 301).—2. From oil of mustard, Zn, and HCl (O.).—3. From oil of mustard and conc. H_2SO_4 (Hofmann, *B.* 1, 182; Rinne, *A.* 168, 262).

Properties.—Liquid with pungent ammoniacal odour. Miscible with water. Strong base. Dissolves ppd. $Cu(OH)_2$ and Ag_2O.

Reactions.—1. Combines with bromine.—2. H_2SO_4 at 140° forms a compound which, on pouring into water, produces oxy-propyl-amine $HO.C_3H_6.NH_2$.

Salts.—$(B'HCl)_2PtCl_4$: monoclinic tables. Changed by boiling into $(B'HCl)_2PtCl_2$ (Liebermann a. Paal, *B.* 16, 530).—$B'_2H_2SO_4$ (Andreasch, *M.* 5, 33).

Di-allyl-amine $C_6H_{11}N$ *i.e.* $(C_3H_5)_2NH$ (111°) (Ladenburg, *B.* 14, 1879).

Tri-allyl-amine $C_9H_{15}N$ *i.e.* $(C_3H_5)_3N$. (156° i.V.) S.G. $\frac{0}{0}$ ·8206. S.V. 200·3 (Zander). C.E. (0°–10°) ·00103. Formed when tetra-allyl-ammonium hydroxide is distilled (C. a. H.; Pinner, *B.* 12, 2054; Grosheintz, *Bl.* 31, 391).—$B'HCl$.—$B'_2H_2PtCl_6$.

Tetra-allyl-ammonium hydrate $(C_3H_5)_4NOH$: liquid. — $((C_3H_5)_4NCl)_2PtCl_4$. — $(C_3H_5)_4NBr$. — $(C_3H_5)_4NI$. The three last are crystalline (C. a. H.).

ALLYL-AMYL-AMINE $C_8H_{17}N$ *i.e.* $(C_3H_5)(C_5H_{11})NH$. (c. 150°). S.G. $\frac{14}{14}$ ·777. From amyl bromide and allyl-amine (Liebermann a. Paal, *B.* 16, 531).

ALLYL AMYL OXIDE $C_8H_{16}O$ *i.e.* $C_5H_{11}.O.C_3H_5$ (120°) (Berthelot a. de Luca, *A. Ch.* [3] 48, 292).

ALLYL-ANILINE $C_9H_{11}N$ *i.e.* $PhN(C_3H_5)H$. (209°). S.G. $\frac{25}{}$ ·982 (Schiff, *A. Suppl.* 3, 364).

Di-allyl-aniline $C_{12}H_{15}N$ *i.e.* $PhN(C_3H_5)_2$. (244°). S.G. $\frac{0}{0}$ ·9680. S.V. 225·2 (Zander, *A.* 214, 149). C. E. (0°–10°) ·00083.

ALLYL-BENZENE C_9H_{10} *i.e.* $Ph.CH:CH.CH_3$(?) *Phenyl-propylene. Propenyl-benzene.* Mol. w. 118. (175°) (P.); (178°) (E.). S.G. $\frac{15}{}$ ·92.

Formation. — 1. By-product in action of sodium-amalgam on warm aqueous cinnamyl alcohol (Fittig a. Krügener, *B.* 6, 214; Rügheimer, *A.* 172, 129).—2. From propyl-benzene by Br at 160° and distilling the product (Radziszewski, *C. R.* 78, 1153): $PhC_3H_6Br = PhC_3H_5 + HBr$. So prepared it boils at (165°), and its di-bromide forms needles.—3. From bromo-hydro-phenyl-crotonic acid (Perkin, *C. J.* 32, 660).—4. From chloro-propyl-benzene and alcoholic potash (Errera, *G.* 14, 504).

Di-bromide $C_9H_{10}Br_2$ [66·5°]. Plates or needles. On distillation it yields an allyl-benzene (178°), which polymerises forming a viscid solid (330°).

Iso-allyl-benzene $Ph.CH_2.CH:CH_2$(?) (155°). Chojnacki (*C. R.* 76, 1413) got this body from allyl iodide or bromide, benzene, and zinc dust at 100°. Others have failed to get it. Allyl chloride, benzene, and Al_2Cl_6 give di-phenyl propane, $CH_3.CHPh.CH_2Ph$, and *n*-propyl-benzene (*q. v.*) (Wispek a. Zuber, *A.* 218, 378).

ALLYL BENZOATE *v.* BENZOIC ACID.

ALLYL-BENZOYL-ACETIC ACID $C_{12}H_{12}O_3$ *i.e.* $BzCH(C_3H_5)CO_2H$ [122°–125°]. From benzoyl-acetic ether, NaOEt, and allyl iodide. The resulting ether is saponified by standing for three weeks with dilute alcoholic KOH (W. H. Perkin, jun., *C. J.* 45, 186; 47, 240). Colourless crystals.

Reaction.—Boiled with dilute alcoholic KOH forms phenyl butenyl ketone (*q. v.*), benzoic acid and (probably) allyl-acetic acid.

Ether.—EtA' (220°) at 100 mm.; (241°) at 225 mm. Combines with Br.

ALLYL BORATE $C_9H_{15}BO_3$ *i.e.* $(C_3H_5)_3BO_3$ (168°–175°). From B_2O_3 and allyl alcohol at 130° (Councler, *J. pr.* [2] 18, 376). Combines with bromine, forming $(C_3H_5Br_2)_3BO_3$.

ALLYL BROMIDE C_3H_5Br *i.e.* $CH_2:CH.CH_2Br$ (71°). S.G. $\frac{0}{0}$ 1·459; $\frac{15}{}$ 1·436. S.V. 90·5 (Zander, *A.* 214, 144). C.E.(0°–10°) ·00123. H.F.p. −340; H.F.v. −1500.

Formation.—1. From allyl alcohol, bromine, and phosphorus (Tollens, *A.* 156, 152).—2. From glycerine and PBr_3 (Henry, *Z.* [2] 6, 575).—3. From allyl iodide and cupric bromide: $2C_3H_5I + 2CuBr_2 = Br_2 + Cu_2I_2 + 2C_3H_5Br$ (Oppenheim, *B.* 3, 442).

Preparation.—Potassic bromide, hydric sulphate (2 pts.), and water (1 pt.) are warmed till hydric bromide begins to come off. Allyl alcohol is then dropped in (Grosheintz, *Bl.* 30, 98).

Combinations.—1. With concentrated *hydric bromide* forms a mixture of propylene bromide ($CH_3.CHBr.CH_2Br$) and trimethylene bromide ($CH_2Br.CH_2.CH_2Br$) which may be separated by distillation (Geromont, *A.* 158, 369).—2. With dry HBr it forms chiefly trimethylene bromide (*q. v.*).—3. With *bromine* it forms tribromhydrin (*q. v.*).—4. With ICl it forms C_3H_5IClBr.—5. With ClBr at 20° forms $C_3H_5ClBr_2$, but at 100° forms $C_3H_5Cl_2Br$ (M. Simpson, *Pr.* 27, 119).—6. With HClO it produces $C_3H_5(OH)BrCl$.—7. It combines with NEt_3.

ALLYL BUTYRATE *v.* BUTYRIC ACID.

ALLYL-ISO-BUTYL-MALONIC ETHER $C_{14}H_{24}O_4$ *i.e.* $(C_3H_5)C(C_4H_9)(CO_2Et)_2$ (247°–250°). From di-sodio-malonic ether, allyl iodide, and iso-butyl iodide (Ballo, *B.* 14, 335). On saponification it gives an acid [129°] which appears to be propyl-iso-butyl-malonic acid.

ALLYL CARBAMINE C_4H_5N *i.e.* $CH_2:CH.CH_2.NC$ (96°–106°). S.G. $\frac{17}{}$ ·794. Produced by the action of silver cyanide on allyl iodide. It is a liquid of disagreeable odour Somewhat soluble in water (Lieke, *A.* 112, 316).

DI-ALLYL CARBINOL v. HEPTINYL ALCOHOL.

DI-ALLYL-DI-CHLORHYDRIN $C_6H_{12}Cl_2O_2$ *i.e.* $C_6H_{10}(OH)_2Cl_2$. From HClO and di-allyl (Przybytek, *B.* 18, 1350; Lauch, *B.* 18, 2288).

ALLYL CHLORIDE C_3H_5Cl *i.e.* $CH_2:CH.CH_2Cl$ (46°) (Thorpe); (44·6°) at 744 mm. (Brühl). S.G. $\frac{0}{0}$ ·9547; $\frac{20}{4}$ ·9379 (Brühl). C.E. (0°-10°) ·00137. S.V. 84·7 (Zander). S.H. ·3984 (Reis). μ_β 1·4225. R_∞ 32·63 (Brühl). H.F.p. 7100. H.F.v. 5940. M.M. 6·008 at 19·6°.

Formation.—1. From allyl iodide and $HgCl_2$. 2. From allyl oxalate, calcic chloride, and alcohol (Oppenheim, *A.* 140, 205).—3. From allyl alcohol and HCl in sealed tubes.

Preparation.—From allyl alcohol and PCl_3 (Tollens, *A.* 156, 154).

Properties.—1. Alcoholic *potash*, even below 100°, converts it into ethyl allyl oxide. The isomeric chloropropylene (26°) is converted by alcoholic potash at 120° into allylene.—2. HClO unites, forming unsymmetrical dichlorhydrin, $CH_2Cl.CHCl.CH_2OH$, or dichloride of allyl alcohol. This body, when oxidised by HNO_3, is converted into dichloropropionic acid (Henry, *B.* 7, 757).—3. HCl combines, forming $CH_3.CHCl.CH_2Cl$.—4. HBr forms $CH_2Br.CH_2.CH_2Cl$, together with a little $CH_3.CHBr.CH_2Cl$.—5. Warmed with H_2SO_4 and then diluted and distilled, propylene chlorhydrin is produced (Oppenheim, *A. Suppl.* 6, 367).—6. *Bromine* combines, forming $C_3H_5Cl.Br_2$.—7. With *potassic cyanide* in presence of dilute alcohol it forms chiefly pyrotartaric acid, also propylene cyanide (Claus, *A.* 191, 38) and triallylamine (Pinner, *B.* 12, 2053). The reactions in this case are: (*a*) $CH_2:CH.CH_2Cl + KCN = KCl + CH_2:CH.CH_2.CN$. (*b*) $CH_2:CH.CH_2CN + HCN = CH_3.CH(CN).CH_2CN$ (*c*) $CH_3.CH(CN).CH_2CN + 2KOH + 2H_2O = 2NH_3 + CH_3.CH(CO_2K).CH_2.CO_2K$ (pyrotartrate). The liberated ammonia forms the triallylamine. 8. With *benzene*, in presence of aluminium chloride, forms diphenylpropane: $C_3H_5Cl + 2C_6H_6 = HCl + (C_6H_5)_2C_3H_6$ (Silva, *C.R.* 89, 606).

ALLYL-PSEUDO-CUMYL-PHTHAL-AMIDE. $C_{20}H_{22}N_2O_2$ *i.e.* $C_6H_2Me_3.NH.CO.C_6H_4.CO.NHC_3H_5$. [179°]. Silky needles. Easily soluble in alcohol. Formed by the action of allylamine on phthal-pseudo-cumidine (Fröhlich, *B.* 17, 1808).

ALLYL CYANAMIDE

$C_4H_6O_2$ ½aq. *i.e.* $(CN.NHC_3H_5)_x$. *Sinamine* [100°]. From allyl-thio-urea and $Pb(OH)_2$ or HgO. (Will, *A.* 52, 15; Andreasch, *M.* 2, 780; Robiquet a. Bussy, *J. pr.* 19, 234). Alkaline. Sol. water, alcohol, and ether. Forms compounds with $HgCl_2$, ½$PtCl_4$, and oxalic acid.

ALLYL CYANATE C_4H_5NO *i.e.* $C_3H_5N.CO$. *Allyl carbimide.* (82°). V.D. 3·05 (for 2·88). From allyl iodide and silver cyanate (Cahours a. Hofmann, *Tr.* 1857, 555).

ALLYL CYANIDE C_4H_5N *i.e.* $CH_2:CH.CH_2CN$. *Crotonitrile.* Mol. w. 67. (119° cor.). S.G. $\frac{0}{0}$ ·8491; $\frac{15}{15}$ ·8351; $\frac{12.9}{0}$: ·8398.

Formation.—1. By ppg. potassic myronate (*q. v.*) with silver nitrate and treating the pp. with hydric sulphide $C_4H_5Ag_2NS_2O_4 + H_2S = C_4H_5N + Ag_2S + S + H_2SO_4$.—2. During the fermentation of black mustard.—3. From allyl mustard oil by zinc dust: $C_3H_5NCS + Zn = ZnS + C_3H_5CN$ (Schwarz, *B.* 15, 2508).—4. From allyl sulphocyanide and sodium (Billeter, *B.* 8, 465).

Preparation.—Allyl iodide is heated with KCy for two days at 110°. The product is washed, dried, and heated again with KCy at 110°. It is then washed, dried over $CaCl_2$, distilled, freed from carbamine by shaking with a little HNO_3, and rectified (Rinne a. Tollens, *A.* 159, 106).

Properties.—Liquid smelling faintly of garlic.

Reactions.—1. Aqueous or alcoholic *potash* forms NH_3, and solid crotonic acid [72°]. The formation of this crotonic acid may be explained by the assumption that β-oxybutyrate is first formed: $CH_2:CH.CH_2CN + KOH + 2H_2O = NH_3 + CH_3.CH(OH).CH_2.CO_2K$, and that this splits off water: $CH_3.CH(OH).CH_2.CO_2K = H_2O + CH_3.CH:CH.CO_2K$, forming potassic crotonate. This view is supported by the behaviour of allyl cyanide towards HCl.—2. With fuming *hydric chloride* at 60° it forms β-chlorobutyric acid: $CH_2:CH.CH_2.CN + 2HCl + 2H_2O = NH_4Cl + CH_3.CHCl.CH_2.CO_2H$. This is an unstable acid, which easily changes to crotonic acid.—3. HNO_3 forms acetic and oxalic acids.—4. CrO_3 forms acetic acid.

Combinations.—1. With *alcohol*. When potassic cyanide acts on allyl iodide in alcoholic solution, a compound of allyl cyanide and alcohol, of boiling point (174°), is obtained: $CH_2:CH.CH_2CN + HOEt = CH_3.CH(OEt).CH_2.CN$. Saponified by strong HCl, this forms ethoxybutyramide, $CH_3.CH(OEt).CH_2.CONH_2$ [71°], which, when warmed with HCl, gives ethoxybutyric acid, $CH_3.CH(OEt).CH_2.CO_2H$, boiling about 215°. Saponified by potash, the compound of allyl cyanide and alcohol (β-ethoxybutyronitrile) gives ordinary crotonic acid as follows: $CH_3.CH(OEt).CH_2.CN + KOH + H_2O = NH_3 + HOEt + CH_3.CH:CH.CO_2K$ (Rinne, *B.* 6, 389). Dry hydrogen chloride converts the compound of allyl cyanide and alcohol into the chloride of β-chlorobutyrimid-ether (166°), $CH_3.CHCl.CH_2.C(OEt)NH$. This last compound is converted by alcoholic potash into crotonic acid (Pinner, *B.* 17, 2007).

2. With *allyl alcohol*. A similar compound, $CH_3.CH(OC_3H_5).CH_2CN$ (96°), is formed when KCy acts on allyl chloride mixed with allyl alcohol.

Constitution.—From its mode of preparation, allyl cyanide ought to be $CH_2:CH.CH_2.CN$, but from its reaction with potash it should be the nitrile of ordinary crotonic acid $CH_3.CH:CH.CN$. From the fact that allyl cyanide and crotonic acid both produce acetic acid on oxidation, while allyl iodide and allyl alcohol yield no acetic acid, Kekulé assumes the presence of a methyl group in the two former and its absence in the two last named (*B.* 6, 386). This reasoning seemed conclusive until the experiments of Pinner, mentioned above, showed that, when the cyanide is converted into crotonic acid by hydric chloride, an intermediate compound (β-chlorobutyric acid) is produced, and it is therefore possible that when nitric or chromic acid is used, an unstable derivative of butyric acid (say, β-oxybutyric acid) is first formed, and that it is this which gives acetic acid on oxidation.

ALLYLENE C_3H_4 *i.e.* Me.C:CH. *Methyl-acetylene. Propinene.* Mol. w. 40. S. (ether) 30 at 16°. H.F.p. −39950 (Thomsen); −37500 (Berthelot). H.F.v. −41530 (Th.).

Formation.—1. By action of alcoholic NaOH upon bromo-propylene (Sawitsch, *C. R.* 52, 399), chloro-propylene, or propylene bromide (Miasnikoff, *A.* 118, 332).—2. By the action of Na upon $CH_3.CCl_2.CHCl_2$ (Borsche a. Fittig, *A.* 133, 111), $CH_2Cl.CCl_2.CH_2Cl$, or $CH_2:CCl.CH_2Cl$ (Pfeffer a. Fittig, *A.* 135, 357).—3. By electrolysis of calcium mesaconate or citraconate (Aarland, *J. pr.* [2] 7, 142).—4. By heating (citra-) bromo-pyrotartaric anhydride with ammoniacal $AgNO_3Aq$ at 130° (E. Bourgoin, *C. R.* 85, 710). Colourless gas, with unpleasant smell; burns with smoky flame. V. sol. alcohol, sol. water.

Reactions.—1. Ammoniacal *cuprous chloride* gives a canary coloured pp.—2. Absorbed by conc. H_2SO_4 much more readily than acetylene, allylene sulphonic acid, $C_3H_3SO_3H$, being produced. An aqueous solution of this acid, when heated, yields mesitylene and acetone (A. Schroke, *B.* 8, 17, 367).—3. Aqueous *mercuric salts* form pps. containing the mercuric salt, HgO, and allylene. These pps. are decomposed by acids with formation of acetone (Kutscheroff, *B.* 14, 1541; *J. R.* 1882, 326).—4. $KMnO_4Aq$ forms, in the cold, malonic, oxalic, and formic acids (Berthelot, *A. Suppl.* 5, 97).—5. CrO_3Aq forms propionic acid (Berthelot, *A. Suppl.* 8, 47).

Metallic Derivatives. — $CH_3.C:CNa$: white powder, decomposed by water into NaOH and allylene (Berthelot, *A. Ch.* [4] 9, 395; *J. R.* 12, 288).—$(C_3H_3)_2Hg$: crystalline pp. formed by passing allylene into Nessler's solution (Kutscheroff, *B.* 17, 25).

Combinations.—1. Cold fuming HCl forms $CH_3.CCl_2.CH_3$; HBr, and HI act similarly.—2. *Bromine* forms di-bromo-propylene (*q. v.*) and tetra-bromo-propane (*q. v.*). *Iodine* acts similarly.

Iso-allylene $CH_2:C:CH_2$. 1. Formed by electrolysis of potassic itaconate (A.).—2. By the action of sodium on di-chloro-propylene, $CHCl:CH.CH_2Cl$ (from symmetrical tri-chlorhydrin, Hartenstein, *J. pr.* [2] 6, 295).

Properties.—A gas that does not pp. ammoniacal silver or cuprous solutions. Forms a tetrabromide.

Di-allylene C_6H_8 or $CH_2:CH.CH_2.CH_2.C:CH$ *Allyl-allylene* (70°). S.G. ^{18} ·858. V.D. 2·79 (for 2·76). Allyl-acetone is converted by PCl_5 into $C_3H_5.CH_2.CCl_2.CH_3$, which is converted by alcoholic KOH into di-allylene (L. Henry, *C. R.* 87, 171).

Reactions.—1. Aqueous *silver nitrate* gives a pp. C_6H_7Ag aq.—2. Ammoniacal *cuprous chloride* gives a canary-yellow pp. C_6H_7Cu aq.—3. Alcoholic $AgNO_3$ gives a pp. $C_6H_7AgEtOH$.—4. *Bromine* forms $C_6H_8Br_6$.

Iso-allylene tetra-carboxylic acid *v.* PROPANE TETRA-CARBOXYLIC ACID.

ALLYLENE DI-CHLORIDE *v.* DI-CHLORO-PROPYLENE.

ALLYLENE OXIDE C_3H_4O (63°). Formed by oxidising allylene with CrO_3Aq (Berthelot, *Bl.* 14, 116). Pungent neutral liquid. Not attacked by baryta-water at 150° or by KOHAq at 300°. Reduces $AgNO_3Aq$.

ALLYL ETHANE *v.* PENTINENE.

ALLYL ETHER *v.* ALLYL OXIDE.

ALLYL ETHYL OXIDE *v.* ETHYL ALLYL OXIDE.

DI-ALLYL HYDRATE *v.* HEXENYL ALCOHOL.

DI-ALLYL-DI-HYDRATE *v.* DI-OXY-HEXANE.

ALLYLIN *v.* GLYCERIN.

ALLYL IODIDE C_3H_5I *i.e.* $CH_2:CH.CH_2I$ (102·7° i. V.). S.G. $\frac{0}{4}$ ·8696. C.E. ·00106. S.V. 100·9 (Zander, *A.* 214, 145); V. D. 5·77 (obs.).

Formation.—1. Allyl alcohol, P, and iodine (Tollens, *Bl.* [2] 9, 396).—2. Glycerin and PI_4 (Berthelot a. de Luca, *A. Ch.* [3] 43, 257).—3. Glycerin distilled with hydriodic acid; excess of the latter is to be avoided, as it would convert the allyl iodide into isopropyl iodide:

$$CH_2:CH.CH_2I + 2HI = CH_3.CHI.CH_2I + HI =$$
$$CH_3.CH:CH_2 + I_2 + HI = CH_3.CHI.CH_3 + I_2$$

(Erlenmeyer, *A.* 139, 211).—4. From allyl chloride and calcic iodide (Romburgh, *R.* 1, 151; Spindler, *A.* 231, 270).

Preparation.—200 grms. of glycerin, previously dried by heating to 280°, are mixed with 125 grms. of iodine. The tubulus of the retort is connected by a flexible tube with a flask containing 40 grms. of clear phosphorus in small pieces; this flask has also a side tube through which carbonic acid is passed until the air is cleared out of the entire apparatus. The clear phosphorus is added to the contents of the retort by tilting the flask from time to time. Allyl iodide distils over rapidly. The addition of phosphorus takes about 2½ hours. The distillation is then continued until the contents of the retort begin to carbonise and vapours of acroleïn are given off. The distillate is washed with dilute NaOH, dried over $CaCl_2$, and rectified. Yield 110 grms. (98°-102°).

Theory of the Process.—It is usually held that triiodhydrin is first formed:

$$CH_2(OH).CH(OH).CH_2(OH) + P + I_3 = H_3PO_3 + CH_2I.CHI.CH_2I,$$

and that this splits up into iodine and allyl iodide: $CH_2I.CHI.CH_2I = I_2 + CH_2:CH.CH_2I$. But the fact that allyl alcohol accompanies the allyl iodide renders it quite likely that the intermediate body is diiodhydrin:

$$CH_2I.CHI.CH_2OH = I_2 + CH_2:CH.CH_2OH.$$

The allyl alcohol formed in this way being converted into iodide by HI (Henry, *B.* 14, 403).

Reactions.—1. *Zinc* and HCl reduce it to propylene.—2. Salts of *silver* form silver iodide and salts of allyl.—3. Dry *hydric iodide* converts it into isopropyl iodide (Simpson, *Pr.* 12, 533). 4. With *zinc ethyl* at 100° it forms amylene, pentane, and diallyl (Wurtz, *C. R.* 56, 387).—5. With *cacodyl* it reacts thus: $As_2Me_4 + 2C_3H_5I = AsMe_2I + AsMe_2(C_3H_5)_2I$ (Cahours, *A. Ch.* [3] 62, 291).—6. With *dry copper zinc couple* at 100° it forms diallyl: $2C_3H_5I + Zn = ZnI_2 + (C_3H_5)_2$.—7. With *wet* copper-zinc couple it forms propylene: $C_3H_5I + H_2O + Zn = IZnOH + C_3H_6$.—8. With *zinc* and alcohol (S.G. ·805) it also forms propylene (Gladstone a. Tribe, *C. J.* 27, 208).—9. With $HgBr_2$ at 200° it gives HgI_2, HBr and propane (Montgolfier a. Girand, *B.* 12, 1211).—10. Heated at 100° for a long time with *water* it forms allyl alcohol (*q. v.*).—11. With KCN and alcohol it forms a di-cyanide which, when boiled with KOH, produces potassic pyrotartrate (Claus, *A.* 191, 38).

Combinations.—1. With *chloride of iodine* it unites, forming $C_3H_5I_2Cl$ (205°-210°), a colourless oil (M. Simpson, *Pr.* 13, 540).—2. *Bromine* forms $C_3H_5Br_3$.—3. *Mercury* unites with it, forming C_3H_5HgI, mercuric-allyl iodide.

ALLYL-MALONIC ACID
$C_6H_8O_4$ *i.e.* $C_3H_5CH(CO_2H)_2$. [103°]. (Conrad a. Bischoff, *B.* 13, 597; *A.* 204, 166; Hjelt, *A.* 216, 52). Large prisms. V. sol. water, alcohol, and ether. At 180° it splits up into CO_2 and allyl-acetic acid. Combines with HBr forming liquid $(CO_2H)_2CH.C_3H_6Br$ which, when boiled with water gives a lactone of oxy-propyl-malonic acid (*q. v.*). Combines with Br_2 forming di-bromo-propyl-malonic acid (*q. v.*).

Salts.—CaA'': crystalline powder.—Ag_2A''.

Ether.—Et_2A'' (218°–225°); (194°) at 330 mm. S.G. $\frac{16}{17}$ 1·018 (C. a. B.); $\frac{15}{15}$ 1·014. M.M. 11·28 at 13·7° (Perkin). From sodio-malonic ether and allyl iodide.

Di-allyl-malonic acid
$C_9H_{12}O_4$ *i.e.* $(C_3H_5)_2C(CO_2H)_2$. [133°]. Rhombic prisms; $a:b:c = \cdot9916:1:1\cdot0179$ (Haushofer, *Z. K.* 11, 147). Sol. water, alcohol, and ether; v. sl. sol. CS_2.

Reactions.—1. *Heat* splits it up into CO_2 and di-allyl-acetic acid.

Ether Et_2A''. (240°) (C. a. B.); (203°) at 225 mm. S.G. $\frac{14}{14}$ ·996 (C. a. B.); $\frac{15}{15}$ 1·000; $\frac{25}{25}$ ·993 (Perkin). M.M. 15 at 22°. From allyl iodide and sodio-malonic ether (Conrad a. Bischoff, *B.* 13, 598; *A.* 201, 171; Hjelt, *A.* 216, 61).

ALLYL MERCAPTAN C_3H_5SH. Mol. w. 74. (90°) (Hofmann a. Cahours, *A.* 102, 292).—C_3H_5SHgCl: pearly plates (from alcohol) (Gerlich, *A.* 178, 88).

ALLYL METHYL ETHER *v.* METHYL ALLYL OXIDE.

ALLYL MUSTARD OIL *v.* ALLYL THIO-CARBIMIDE.

ALLYL NITRATE $C_3H_5NO_3$. (106°). S.G. $\frac{12}{}$ 1·09. V.D. 3·54 (for 3·56). From allyl bromide and $AgNO_3$ (Henry, *B.* 5, 452).

ALLYL NITRITE $C_3H_5NO_2$ *i.e.* $C_3H_5.O.NO$. (44°). S.G. $\frac{0}{}$ ·955. Prepared by distilling glyceryl tri-nitrite with allyl alcohol. An oil. Decomposed by MeOH into allyl alcohol and methyl nitrite. Its vapour explodes at 100° (Bertoni, *G.* 15, 361).

ALLYL OXALATE *v.* OXALIC ACID.

DI-ALLYL-OXALIC ACID (so called) *v.* OXY-OCTINOIC ACID.

DI-ALLYL-OXAMIDE $C_8H_{12}N_2O_2$ *i.e.* $C_3H_5NH.CO.CO.NHC_3H_5$. [154°]. (274°). White plates. Soluble in hot water. Prepared by the action of allylamine on oxalic ether.

Tetrabromide $C_2O_2(NHC_3H_5Br_2)_2$. Insoluble in most ordinary solvents, except hot acetic acid (Wallach a. Stricker, *B.* 13, 513).

DI-ALLYL OXIDE $C_6H_{10}O$ *i.e.* $(C_3H_5)_2O$. *Allyl ether.* Mol. w. 98. (82°) (Cahours a. Hofmann, *A.* 102, 290); (94·3° i.V.) (Zander, *A.* 214, 146). S.G. $\frac{0}{0}$ ·8223. S.V. 135·5. C.E. (0°–10°) ·00127. H.F.p. 12460. H.F.v. 9850 (Thomsen).

DI-ALLYL DI-OXIDE

$$\overset{\diagup O \diagdown}{CH_2 \,.\, CH}.CH_2.CH_2.\overset{\diagup O \diagdown}{CH \,.\, CH_2}$$

(180°). V.D. = 3·7 (obs.). Mobile colourless fluid of slight smell and burning taste. Heavier than water. Combines with acids, and pps. magnesia from a solution of $MgCl_2$. Obtained by the action of solid caustic alkalis upon di-allyl-di-chlorhydrin. By boiling with water it is converted into the alcohol-oxide

$$\overset{\diagup O \diagdown}{CH_2 \,.\, CH}.CH_2.CH_2.CH(OH).CH_2(OH),$$

which only by long heating with water is converted into the tetra-hydric alcohol
$CH_2(OH).CH(OH).CH_2.CH_2.CH(OH).CH_2(OH)$ (Przybytek, *B.* 18, 1350).

o - **ALLYL - PHENOL.** *Methyl derivative* $C_{10}H_{12}O$ *i.e.* $C_6H_4(OMe).CH_2.CH:CH_2$. (233°). S.G. $\frac{15}{15}$ ·9972; $\frac{30}{30}$ ·9884; $\frac{45}{45}$ ·9793. Formed by the action of Na_2CO_3Aq on the product of the union of HI with the methyl derivative of (α)- or (β)-oxy-phenyl-crotonic acid (*q. v.*). It is an oil; combines with bromine; forms a red solid with H_2SO_4 (Perkin, *C. J.* 39, 425).

p - Allyl-phenol. *Methyl derivative.* (232°) S.G. $\frac{30}{30}$ ·985. Prepared as above from corresponding *p*-compound. Anethol (*q. v.*) is isomeric with this body. Anol (*q. v.*) is isomeric with allyl-phenol.

ALLYL-PHENYL-THIO-UREA $C_{10}H_{12}N_2S$ *i.e.* $C_3H_5.NH.CS.NHPh$. [98°]. S. (alcohol) 71 at 18°. From oil of mustard and aniline (Zinin, *A.* 84, 348); from allyl-amine and phenyl thio-carbimide (Weith, *B.* 8, 1529). Monoclinic crystals; v. sol. ether, insol. water. Cyanogen passed into an alcoholic solution forms $C_{10}H_{12}N_2S(CN)_2$, ppd. by water (Maly, *Z.* 1869, 261). When this is warmed with alcohol and dilute H_2SO_4 it forms the oxalyl derivative.

Oxalyl Derivative

$$\begin{array}{l} CO.NC_3H_5 \diagdown \\ | \qquad\qquad\quad CS \\ CO.NC_6H_5 \diagup \end{array}$$

[161°]. Lemon-yellow needles, insol. water, sl. sol. cold alcohol.

ALLYL-PHENYL-UREA $C_{10}H_{12}N_2O$ *i.e.* $C_3H_5.NH.CO.NHPh$. [97°]. Needles. Got from its oxalyl derivative by baryta (Maly, *Z.* 1869, 263).

Oxalyl-derivative
$$\begin{array}{l} CO-NC_3H_5 \diagdown \\ | \qquad\qquad\quad CO. \\ CO-NC_6H_5 \diagup \end{array}$$

From the oxalyl derivative of allyl-phenyl-thio-urea (*q. v.*) and warm $AgNO_3$ in alcoholic solution. Long needles. Insol. water, v. sol. alcohol, benzene, and CS_2.

ALLYL-PHTHALIMIDE *v.* PHTHALIC ACID, *Allylamide.*

ALLYL - PROPYL ALCOHOL *v.* HEXENYL ALCOHOL.

ALLYL-PROPYL-AMINE $C_6H_{13}N$ *i.e.* $C_3H_5NHC_3H_7$. (c. 112°). S.G. $\frac{18}{18}$ = ·7708. Colourless fluid. S. = about 6. Prepared by the action of propyl bromide on allylamine.

Salts: $B'_2H_2Cl_2PtCl_4$: orange crystals.—$B'H_2C_2O_4$: sl. sol. needles.—$B'_2H_2C_2O_4$: thin plates (Liebermann a. Paal, *B.* 16, 525).

Allyl-di-propyl-amine $(C_3H_7)_2NC_3H_5$. (c. 147°). Colourless fluid. S = about 2. Formed by the action of propyl bromide on allylamine.

Salts.—$B'_2H_2Cl_2PtCl_4$: orange-red trimetric crystals, $a:b:c = \cdot9831:1:1\cdot1217$. $B'HClPtCl_2$: sparingly soluble yellow needles [152°]; formed by boiling the preceding salt with water (Liebermann a. Paal, *B.* 16, 527).

ALLYL-ISO-PROPYL-BENZENE *v.* PROPENYL-ISO-PROPYL-BENZENE.

ALLYL DI-PROPYL CARBINOL *v.* DECENYL ALCOHOL.

Di-allyl propyl carbinol *v.* DECINYL ALCOHOL.

a-ALLYL-PYRIDINE $C_5H_4(C_3H_5)N$. (c. 190°).

S.G. $\frac{0}{}$ ·9595. Colourless refractive oil; sl. sol. water. Prepared by heating pure (α)-picoline with paraldehyde for 10 hours at 250°-260°. On oxidation it gives picolinic acid [133°]. On reduction in alcoholic solution by means of sodium it yields (α)-propyl-pyridine (inactive coniine).

Salts.—$(B'HCl)_2PtCl_4$: [186°], sparingly soluble needles.—$B'HClAuCl_3$˟ : [136°], oily pp. solidifying to small needles.—$(B'HCl)_2HgCl_2$˟ : very sparingly soluble crystalline pp. (Ladenburg, *B.* 19, 2578).

ν-ALLYL-PYRROL C_7H_9N *i.e.* $C_4H_4N.C_3H_5$. [105°] at 48 mm. Formed by the action of allyl bromide on pyrrol-potassium. Colourless oil. Volatile with steam. Almost insoluble in water. $HgCl_2$ gives a white pp. (Ciamician a. Dennstedt, *B.* 15, 2581; *G.* 13, 17).

ALLYL-RESORCIN $C_6H_3(C_3H_5)(OH)_2$. *Monomethyl ether* $C_6H_3(C_3H_5)(OMe)(OH)$. (245°-250°); V.D. 165 (obs.); colourless oil (Pechmann a. Cohen, *B.* 17, 2132).

ALLYL-SUCCINIC ACID

$C_7H_{10}O_4$ *i.e.* $CO_2H.CH_2.CH(C_3H_5).CO_2H$.

[94°]. Plates (from alcohol). Prepared by heating allyl-ethane tri-carboxylic acid to 160°, CO_2 being evolved. Strong aqueous HBr converts it into the corresponding lactonic acid—

$$\begin{array}{l}CH_3.CH.CH_2.CH.CH_2.CO_2H\\ \quad\ \ |\qquad\qquad\ |\\ \quad\ \ O\ \text{———}\ CO\end{array}$$

Salts: A″Ca˟ : crystalline, soluble.—A″Ba˟ : easily soluble, amorphous.—$A''Ag_2$˟ : sparingly soluble, amorphous.—$FeSO_4$ gives a flocculent pp. (Hjelt, *B.* 16, 334).

ALLYL SULPHATE $C_3H_6SO_4$ *i.e.* $C_3H_5O.SO_2.OH$. *Hydrogen allyl sulphate. Allyl-sulphuric acid.* From allyl alcohol and H_2SO_4 (Cahours a. Hofmann, *C. J.* 10, 316).

Salts.—(Szymanski, *A.* 230, 43.) BaA'_2.—SrA'_2.—CaA'_2 2aq.—CuA'_2 4aq.—PbA'_2PbO 6aq.—MgA'_2 4aq.—KA′.—NaA′.—NH_4A'.

ALLYL SULPHIDE $C_6H_{10}S$ *i.e.* $(C_3H_5)_2S$. *Oil of Garlic.* M. w. 114. (140°).

Occurrence.—In the essential oils obtained by distilling, with steam, the leaves, seeds, or bulbs, of various plants (*allium sativum, alliaria officinalis, allium cepa, thlaspi arvense*). Often associated with allyl-thio-carbimide (*q.v.*) (Wertheim, *A.* 51, 289; 55, 297; Pless, *A.* 58, 36).

Formation.—From allyl iodide and alcoholic K_2S (Hofmann a. Cahours, *A.* 102, 291).

Properties.—A light oil, smelling of garlic.

Combinations.—1. Forms pps. with salts of Au, Hg, Pd, Pt, and Ag.—$(C_3H_5)_2SPtS_2$ (W.)—$(C_3H_5)_2SAgNO_3$ (Ludwig, *A.* 139, 121). $HgS(HgCl_2)_3 2(C_3H_5)_2S$ (W.)

2. Combines with MeI (Cahours, *Z.* 1865, 438).

ALLYL SULPHOCYANIDE C_4H_5NS *i.e.* $C_3H_5.S.CN$. *Allyl thio-cyanate.* (161°). S.G. $\frac{0}{}$ 1·071; $\frac{15}{}$ 1·056.

Formation.—1. From lead salt of allyl mercaptan and cyanogen chloride in ethereal solution (Billeter, *B.* 8, 464):

$(C_3H_5S)_2Pb + 2Cl(CN) = 2C_3H_5.S.CN + PbCl_2$.

2. From ammonium sulphocyanide and a cold alcoholic solution of allyl bromide (Gerlich, *A.* 178, 85).

Properties.—Changes spontaneously into the isomeric allyl-thio-carbimide, especially when boiled. Alcoholic KOH forms KSCN. Does not give immediate pps. with ammoniacal $AgNO_3$ or alcoholic $HgCl_2$. Zn and HCl in alcohol form $(C_3H_5)_2S$ and HCN (G.). *Sodium amalgam* forms Na_2S and allyl carbamine (B.).

ALLYL-SULPHONIC ACID *v.* PROPYLENE SULPHONIC ACID.

ALLYL SULPHYDRATE *v.* ALLYL MERCAPTAN.

ALLYL-TAURINE $C_5H_{11}NSO_3$ *i.e.* $C_3H_5NH.CH_2.CH_2.SO_3H$. [190°-195°]. From $CH_2Cl.CH_2.SO_3H$ and allylamine at 160° (James, *C. J.* 47, 369). Prisms (from alcohol). V. e. sol. water.

ALLYL-THIO-CARBAMIC ACID *Ethyl ether* $C_6H_{11}NSO$ *i.e.* $C_3H_5NH.CS.OEt$. *Allyl-thio-urethane* (210°-215°). S.G. $\frac{14}{}$ 1·036. From oil of mustard and alcohol at 110°:

$C_3H_5N:CS + HOEt = C_3H_5NH.CS.OEt$

(Hofmann, *B.* 2, 119). Ppd. by $HgCl_2Aq$.

Allyl-di-thio-carbamic acid $C_3H_5NH.CS.SH$. From allyl thio-carbimide and alkaline sulphydrates: $C_3H_5N:CS + HSK = C_3H_5NH.CS.SK$. The free acid is unstable.

Salts.—NH_4A' : unstable laminæ.—KA′: large rhombic plates.—NaA′ 3aq: unstable nacreous laminæ.—BaA'_2 4aq: laminæ; v. sol. water.—PbA'_2: white pp. (Will, *A.* 52, 30).

ALLYL THIO-CARBIMIDE C_4H_5NS *i.e.* $C_3H_5N:CS$. *Oil of mustard, allyl mustard oil, allyl thio-cyanate, allyl iso-thio-cyanate, allyl sulphocyanide, allyl iso-sulpho-cyanide, allyl sulpho-carbimide.* M. w. 99. (151°). S.G. $\frac{0}{}$ 1·028. S.V. 113·12 (R. Schiff, *B.* 19, 568). H.F.p. −45,540. H.F.v. −46,700. V.D. 3·54 (for 3·42).

Occurrence.—In the oil distilled from the seeds of black mustard (*sinapis nigra*). Also present in oil of garlic, and in horse-radish.

Formation.—1. Seeds of black mustard contain potassic myronate, and also an unorganised nitrogenous ferment, myrosin. When treated with water, the ferment splits up the potassic myronate thus:

$C_{10}H_{18}NS_2O_{10}K = C_3H_5.NCS + C_6H_{12}O_6 + KHSO_4$.

At low temperatures a little allyl sulphocyanide is also formed (E. Schmidt, *B.* 10, 187).—2. Allyl sulphocyanide (*q. v.*) changes, slowly at 15°, quickly on boiling, into allyl thio-carbimide. Consequently, when allyl iodide is distilled with alcoholic potassic sulphocyanide (Zinin, *A.* 95, 128; Berthelot a. De Luca, *A. Ch.* [3] 44, 495), or allyl sulphide (Wertheim, *A.* 55, 297), the product is allyl thio-carbimide.

Properties.—Oil with pungent odour and burning taste. Blisters the skin. Sl. sol. water, v. sol. alcohol or ether. Slowly decomposed by water, sulphur being liberated.

Reactions.—1. *Zinc and hydric chloride* reduce it to allylamine and thio-formic aldehyde: $C_3H_5NCS + 2H_2 = C_3H_5NH_2 + H_2CS$, the latter being partly reduced to methane and H_2S (Hofmann, *B.* 1, 179).—2. HClAq at 200° forms allylamine, CO_2, and H_2S (H.).—3. *Alcohol* at 100°, or *alcoholic potash*, forms allyl-thio-carbamic ether (*q. v.*).—4. *Aqueous alkalis*, or *water* and the oxides BaO, PbO, Ag_2O, or HgO, form di-allyl-urea: $2C_3H_5NCS + 3PbO + H_2O = (C_3H_5)_2N_2H_2CO + 2PbS + PbCO_3$.—5. K_2S at 100° forms potassic sulphocyanide and allyl-sulphide.—6. NH_3 forms allyl-thio-urea (*thio-sinamine*).—7. *Aldehyde-ammonia* forms needles of $C_{14}H_{31}N_5S_2O_2$ [108°] (R. Schiff *B.* 9, 571).—8. *Furfuramide* in alcoholic solution at

100° forms $C_{14}H_{12}N_2O_2C_3H_5NCS$ [118°] (R. Schiff, *B.* 10, 1191).—9. Boiling conc. $KHSO_3$ forms $C_3H_5NH.CS.SO_3K$. Pearly plates (form alcohol) (Böhler, *A.* 154, 59).

Combination.—$C_3H_5NCS\,Ag_2SO_4$. Formed by adding $AgNO_3Aq$ to aqueous potassic myronate (Will a. Körner, *A.* 125, 2[illegible]7).

Additional References.—Boutron a. Robiquet, *J. Ph.* 17, 296; Henry a. Plisson, *J. Ph.* 17, 451; Dumas a. Pelouze, *A. Ch.* [2] 53, 181; Aschoff, *J. pr.* 4, 314; Robiquet a. Bussy, *A. Ch.* [2] 72, 328; Boutron a. Fremy, *J. Ph.* 16, 112; Löwig a. Weidmann, *J. pr.* 19, 218; Will, *A.* 52, 1; Gerhardt, *A. Ch.* [3] 14, 125; Hubatka, *A.* 47, 153; Vollrath, *J.* 1871, 408; Grabowski, *A.* 138, 173.

ALLYL-THIO-HYDANTOIN $C_6H_8N_2SO$ *i.e.*

$$HN:C\begin{array}{l}\diagup N(C_3H_5)\cdot CO\\ \qquad\qquad\quad |\\ \diagdown S\text{———}CH_2\end{array}$$

Formation.—(1) By the action of chloro-acetic acid on allyl-thio-urea in aqueous solution at 100°. (2) By the action of allyl-cyanamide on thio-glycollic acid.

Minute needles. Sol. hot, sl. sol. cold, water.

The hydrochloride (B'HCl) forms glistening prisms. (Andreasch, *B.* 15, 326; *M.* 2, 775).

ALLYL-THIO-PARABANIC ACID *v.* THIO-PARABANIC ACID.

ALLYL-THIO-URAMIDO-BENZOIC ACID. $C_{11}H_{12}N_2SO_2$ *i.e.* $C_3H_5NH.CS.NH.C_6H_4.CO_2H$. [1:3] [189° uncor.]. Formed by boiling *m*-amido-benzoic acid with an alcoholic solution of allyl-thio-carbimide. Plates. (Aschan, *B.* 17, 431.)

ALLYL-THIO-UREA. $C_4H_8N_2S$ *i.e.* $C_3H_5NH.CS.NH_2$. *Thiosinamine.* M. w. 116. [74°].

Formation.—From allyl mustard oil and ammonia (Dumas a. Pelouze, *A. Ch.* [2] 53, 181; Aschoff, *J. pr.* 4, 314; Löwig a. Weidmann, *J. pr.* 19, 218; Robiquet a. Bussy, *J. pr.* 19, 232; Will, *A.* 52, 1).

Properties.—Prisms, without smell. M. sol. water, v. sol. alcohol, and ether.

Reactions.—1. HgO or PbO converts it into allyl-cyanamide (*q. v.*).—2. Warm $AgNO_3Aq$ forms allyl-urea.

Combinations. — $(C_4H_8N_2S\,HCl)_2PtCl_4$. — $C_4H_8N_2S2HgCl_2$: curdy white pp.—$C_4H_8N_2SAgNO_3$. —$C_4H_8N_2\,SBr_2$ [147°], six-sided columns; sol. water, and alcohol. Converted by moist Ag_2O into alkaline $C_4H_8N_2S\,BrOH$, whence HCl forms $C_4H_8N_2SBrCl$ [130°]. (Maly, *Z.* 1867, 42).— $(C_4H_8N_2SBr_2)_2PtCl_4$. — $(C_4H_8N_2SBrCl)_2PtCl_4$. — $C_4H_8N_2SBrClAuBr_3$. — $C_4H_8N_2SI_2$ [90°]. — $C_4H_8N_2SClI$.—$C_4H_8N_2SCy_2$: converted by hot dilute H_2SO_4 into allyl-THIO-PARABANIC ACID (*q. v.*). (Maly, *Z.* 1869, 259).—$C_4H_8N_2SICyAgCy$.

Ethyloiodide $C_4H_8N_2SEtI$. [72°] (Welzien, *A.* 94, 103; M.).

ALLYL-UREA $C_4H_8N_2O$ *i.e.* $C_3H_5NH.CO.NH_2$. *Allyl carbamide.* [85°]. *Formation.*—1. From allyl cyanate and hot NH_3Aq (Hofmann a. Cahours, *Tr.* 1857, 555).—2. From allylamine sulphate and potassic cyanate (Andreasch, *M.* 5, 34).—3. From allyl thio-urea and $AgNO_3Aq$, the liberated HNO_3 being neutralised by baryta. The yield is 92 p.c. of the theoretical.

Properties.—Needles. V. e. sol. water, and alcohol, v. sl. sol. $CHCl_3$, and ether. Br_2 forms di-bromo-propyl-urea.—Salt.—$B'HNO_3$.

Di-allyl-urea $(C_3H_5NH)_2CO$. *Sinapoline.* [100°].

Formation.—1. By action of water and PbO or baryta on allyl thio-carbimide (Simon, *P.* 50, 377; Will, *A.* 52, 25).—2. By heating allyl cyanate with water or aqueous potash.

Properties.—Unctuous shining laminæ. V. sol. alcohol, ether or hot water; volatile with steam. Its aqueous solution is ppd. by $HgCl_2$ and $PtCl_4$. Dry HCl liquefies sinapoline forming B'HCl.

ALMONDS.—Bitter almonds contain a glucoside, amygdalin (*q. v.*), and a nitrogenous unorganised ferment, emulsin. Sweet almonds contain amygdalin but not emulsin. When bitter almonds are ground up with cold water, the amygdalin is split up by emulsin:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6.$$

The *essential oil* of bitter almonds is obtained by distilling the product with steam. It contains benzoic aldehyde, prussic acid and mandelonitrile, the product of their union. The presence of mandelonitrile is indicated by the formation of phenyl-ethylamine when the oil is acted upon by nascent hydrogen (Fileti, *G.* 9, 446). Both sweet and bitter almonds yield by pressure a *fixed oil*, S.G. $\frac{15}{\,}$ ·913; this consists of oleïn with some stearin and palmitin. It is called *oil of almonds*.

ALNEÏN.—A golden yellow colouring matter in the alder, birch, and beech (Savigny a. Collineau, *C. C.* 1881, 703; *C. J.* 42, 309).

ALOES.—The thickened juice of various species of aloe.

ALOETIC ACID $C_{14}H_4N_4O_{10}$ aq, *i.e.* $C_{14}H_4(NO_2)_4O_2aq$(?). *Tetra-nitro-anthraquinone*(?) Obtained, together with chrysammic acid, by warming aloes with HNO_3 (Schunck, *A.* 39, 24; 65, 235; G. J. Mulder, *A.* 72, 286; Finck, *A.* 134, 236). Yellow amorphous powder. Sl. sol. cold water, m. sol. hot water or alcohol, forming purple solutions, which become yellow on addition of acids, and red again when neutralised. It has a bitter taste. Boiling HNO_3 converts it into chrysammic acid, and ultimately into picric acid. Warm *potassium* or *ammonium sulphide* containing excess of alkali forms an indigo-blue gelatinous mass. **Salts:** $BaC_{14}H_2N_4O_{10}$. Ag_2A'': insoluble, dark red powder.

ALOÏN.—The purgative principle in aloes. There are several varieties classified by Shenstone (*Ph.* [3] 13, 461) as follows: (1) *Nataloïns.*—Are not reddened by HNO_3, but converted by it into picric and oxalic acids.—(2) *Barbaloïns*—are reddened by HNO_3, aloetic, chrysammic, picric and oxalic acids being formed. These may be subdivided into (α)-*barbaloïns*, reddened by cold HNO_3 (S.G. 1·4), (β)-*barbaloïns*, reddened by fuming HNO_3, not by cold HNO_3 (S.G. 1·4). The aloïns may be extracted by hot water or hot spirit from the various aloes, and purified by re-crystallisation. They dissolve in caustic and carbonated alkalis, forming orange solutions. Their solutions are ppd. by lead subacetate.

(α)-Barbaloïn, $C_{16}H_{18}O_7$ and (β)-Barbaloïn, Zanzaloïn or Socaloïn $C_{16}H_{18}O_7$, occur in aloes from Barbadoes, Socotrina, Zanzibar and Jafferabad (T. a. H. Smith, *Chem. Gaz.* 1851, 107; Stenhouse, *P.M.* [3] 37, 481; Tilden, *C. J.* 25, 488; 28, 1270).

Reactions.—1. By distilling with *zinc dust* a very little methyl-anthracene may be got (E.

Schmidt, *B.* 8, 1275).—2. *Potash-fusion* gives orcin, *p*-oxybenzoic acid, and alorcinic acid.—3. Boiling *dilute sulphuric acid* forms *p*-coumaric acid.—4. HCl and $KClO_3$ form tri-chloro-aloïn, $C_{16}H_{15}Cl_3O_7$, yellow prisms (from alcohol).—5. *Bromine* forms tri-bromo-aloïn; yellow needles (from alcohol).—6. Ac_2O forms tri-acetyl-aloïn, $C_{16}H_{15}Ac_3O_7$: amorphous.

Nataloïn $C_{16}H_{18}O_7$ (?). Occurs in Cape aloes (Flückiger, *Ar. Ph.* [2] 149, 11; *Bl.* 17, 328; Tilden, *C. J.* 25, 153). Thin bright yellow scales; sl. sol. water, benzene, ether, CS_2, and $CHCl_3$. Its solution in H_2SO_4 is turned green by KNO_3, the colour changing through red to blue.

Additional References.—T. B. Groves, *Ph.* 16, 128; Orlowski, *Fr.* 5, 309; Hlasiwetz, *A.* 134, 287; Rembold, *A.* 138, 186; Bornträger, *Fr.* 20, 234; R. H. Groves, *Ph.* [3] 11, 1045; Lenz, *Fr.* 21, 220; Plenge, *Ph.* [3] 15, 330; Cripps a. Dymond, *Ph.* [3] 15, 633).

ALORCIC ACID $C_9H_{10}O_3$ aq. [97°]. $C_9H_{10}O_3$ [115°] *i.e.* $C_6H_2(OH)Me_2.CO_2H$. Formed in small quantity, along with *p*-oxy-benzoic acid and orcin, by fusing aloes with KOH (Weselsky, *A.* 167, 65). Long needles. Sl. sol. cold water, v. sol. hot water, alcohol, and ether. The aqueous solution is not coloured by Fe_2Cl_6Aq, but alkaline solutions are turned cherry-red by air. *Hypochlorites* turn the aqueous solution of the acid purple-red, colour destroyed by excess. Basic, but not neutral, *lead acetate* gives a pp. Alorcic acid reduces *silver nitrate* and *Fehling's solution.* Fused with *potash* it forms orcin and K_2CO_3.

Salts. BaA'_2 6aq: small needles.—CaA'_2: needles—CuA'_2 4aq.

Acetyl derivative $C_9H_9AcO_3$: [125°]; needles.

Anhydride $C_9H_8O_2$: [138°]; formed by distilling the acid.

ALOXANTHIN $C_{15}H_{10}O_6$ *i.e.* $C_{14}H_3Me(OH)_4O_2$. From barbaloïn and socaloïn, but not from nataloïn, by chromic mixture. Reduced, by distillation with *zinc dust*, to methyl-anthracene. Its alkaline solutions are cherry-red. *Nitric acid* converts it into aloetic and chrysammic acids (Tilden, *Ph.* [3] 8, 231; *C. J.* 32, 903). It forms an acetyl derivative $C_{15}H_9AcO_6$.

ALPHA. To find compounds beginning with this prefix, remove the prefix and look for the remaining word.

ALPININ $C_{17}H_{12}O_6$. [174°]. Light yellow needles ($+H_2O$). Occurs, together with camphoride and galangin in the galanga-root (Jahns, *B.* 14, 2810).

ALSTONIDINE. [181°]. An alkaloid occurring along with alstonine (*q. v.*) and porphyrine (*q. v.*) in the bark of *Alstonia constricta*. It may be separated from porphyrine by its more sparing solubility in petroleum. It crystallises in radiating needles, sol. alcohol, chloroform, and ether. Its solutions display intense blue fluorescence. It is not coloured by conc. H_2SO_4 or HNO_3. Its salts crystallise in colourless needles. The gold and platinum salts are golden flocculent pps. (Hesse, *A.* 205, 368).

ALSTONINE $C_{21}H_{20}N_2O_4$ 3½aq. *Chlorogenine* (F. v. Müller a. L. Rummel, *C. J.* 35, 31; Oberlin a. Schlagdenhauffen, *Ph.* [3] 10, 1059; O. Hesse, *A.* 205, 360). An alkaloid in the bark of *Alstonia constricta* (F. v. M.), from which it may be extracted by alcohol. The extract is evaporated, treated with very dilute HCl, filtered, ppd. by NH_3, dissolved in ether and evaporated.

Properties.—Orange-yellow, brittle, pellucid, bitter, mass. It melts below 100°. When dry, it melts at 195°. It dissolves easily in alcohol, ether, chloroform, and dilute acids, but sparingly in water. All dilute solutions show blue fluorescence. Salts. Ppd. by excess of acid.—$(B'HCl)_2PtCl_4$ 4aq.—$(B'HCl)_2HgCl_2$.—$B'_2H_2Cr_2O_7$.

ALUMINA.—Oxide of Aluminium, Al_2O_3, *v.* ALUMINIUM, OXIDE OF.

ALUMINATES.—Certain minerals are known, *e.g.* Al_2O_3MgO, Al_2O_3BeO, &c., which may be regarded as derived from the hydrate $Al_2O_3.H_2O$ (*v.* ALUMINIUM, HYDROXIDES OF), by replacing H_2 by Mg, Be, &c. Some of these minerals have been prepared by Ebelmen (*A. Ch.* [3] 22, 211) by dissolving Al_2O_3 and the other metallic oxide in molten boric acid, and removing part of the solvent by long-continued heating; in this way he prepared spinelle Al_2O_4Mg, chrysoberyl Al_2O_4Be, &c. By heating Al_2F_6 with boric acid and ZnF_2, Deville and Caron obtained gahnite Al_2O_4Zn.

Barium aluminate $Al_2O_4Ba.4H_2O$ was obtained in crystals by fusing Al_2O_3 and carbon with BaO, $BaCO_3$, $Ba2NO_3$, or $BaSO_4$, dissolving in water and crystallising (Deville, *C. R.* 54, 327; *v.* also Gaudin, *C. R.* 54, 687; also Beckmann, *J. pr.* [2] 26, 388 a. 474). Compounds of Al_2O_3 and BaO obtained by action of BaOAq on Al_2O_3 and Al_2Cl_6Aq are described by Beckmann (*B.* 14, 2151).

Potassium aluminate $Al_2O_4K_2.3H_2O$ was obtained in crystals by Fremy (*A. Ch.* [3] 12, 362) by fusing Al_2O_3 and KOH in a silver dish, dissolving in water, and evaporating *in vacuo*; this salt may be recrystallised from *con.* aqueous solutions, from dilute solutions $Al_2O_6H_6$ separates out.

Sodium aluminate has not been obtained crystallised. An impure salt is used in manufactures; it is obtained by heating cryolite and CaO, or bauxite and NaOH, in steam, dissolving in water and evaporating to dryness (Morin, *J.* 1862. 668). Tissier (*C. R.* 48, 627) described four compounds to which he assigned the compositions $Al_2O_6Na_6$, $Al_4O_9Na_6$, $Al_2O_5Na_4$, and $Al_2O_4Na_2$; but no analyses are given in the original paper.

M. M. P. M.

ALUMINIUM.—Al. At w. 27·02 (Mallet, *T.* 171, 1003). Mol. w. unknown as V.D. has not been determined. [About 700°]. S.G. $\frac{4°}{4°}$ (fused) 2·583 (Mallet, *T.* 171, 1003); (after pressure of 6,000 atmos.) 2·562 (Spring, *A. Ch.* [5] 22, 170). S.H. ·218 (Louguinine, *A. Ch.* [5] 27, 398); (0°-100°) ·2253 (Mallet, *l.c.*). C.E. (lin. at 40°) ·002313; (lin. 50°) ·002336 (Fizeau, *C. R.* 68, 1125) T.C. (Ag = 100) 31·33 (Lorenz, *W.* 13, 422). E.C. (Hg at 0° = 1) 20·97 at 0°, 16·15 at 15° (Lorenz, *l.c.*). S.V.S. 10·4. Chief lines in spectrum, 3960·9, 3943·4, 3612·4, 3091·9, 3081·2, 2815·3, 2630·6 (Hartley, *T.* 175, 101).

Occurrence.—The metal aluminium does not occur native; but as silicate (in all clays and in very many minerals, especially the felspars), and oxide (corundum, diaspore, &c.), and fluoride (cryolite), it is very widely and largely distributed, forming nearly $\frac{1}{12}$ of the earth's crust. Alumina was shown to be a distinct earth by Marggraff in 1754; the metal was separated by Wöhler in

1828 (*P.* 11, 146), and in purer form in 1854 (*A.* 53, 422).

Preparation.—Wöhler decomposed Al_2Cl_6 by K; in 1854 Deville employed Na and decomposed $2NaCl.Al_2Cl_6$ (*J. pr.* 61, 83, 113, 219, 386). Bunsen (*P.* 92, 648) decomposed fused $2NaCl.Al_2Cl_6$ by an electric current. Rose (*P.* 96, 152) decomposed $6NaF.Al_2F_6$ (cryolite) by fusing it with KCl and Na. Basset (*J.* 1869. 753) reduced $2NaCl.Al_2Cl_6$ by Zn, and heated the Zn-Al alloy to white heat to remove the Zn. The Al_2Cl_6 may also be reduced by KCN (Wagn, *J.* 1858. 1); a compound of Al and S may be reduced by Fe, or by hydrocarbons (Petitjean, *J.* 1858. 136); and in other ways. The usual method of preparation is to heat $2NaCl.Al_2Cl_6$ with about 36 p.c. Na and 40 p.c. cryolite (as a flux), on the hearth of a reverberatory furnace, and to run off the molten Al into iron moulds. The $2NaCl.Al_2Cl_6$ is prepared by heating bauxite (silicate of Al containing Fe) with Na_2CO_3, whereby Na aluminate is formed, dissolving in water, ppg. Al_2O_3 by a stream of CO_2, collecting, washing, and drying the Al_2O_3, mixing it with charcoal and NaCl and heating strongly in Cl whereby $2NaCl.Al_2Cl_6$ is formed and distilled off into receivers. Mallet (*T.* 171, 1003), prepared very pure Al by fusing Al_2Br_6 with KCl and NaCl in the ratio $2(KCl.NaCl):Al_2Br_6$, and then heating with Na in clay crucibles lined with Al_2O_3 and Na aluminate; the reduced metal was heated on a support of Al_2O_3, washed with HClAq, then with water, and dried at a gentle heat.

Properties.—A tin-white metal; grey when in powder. Odourless and tasteless. After fusion about as hard as silver; hammered metal is about as hard as soft iron. Very malleable, and ductile; very sonorous; may be highly polished. Tenacity nearly equal to that of Cu (V. Burg, *D.P.J.* 151, 286); less than that of Zn (Karmarsch, *D.P.J.* 152, 441; 172, 55). Very feebly magnetic. Melts fairly easily (about 700°) and crystallises, apparently in regular octahedra, on cooling. Non-volatile, and non-oxidisable in air; heated in oxygen becomes covered with film of Al_2O_3. Unacted on by H_2S or ammonium sulphides, and by S only at high temperatures. Scarcely attacked by HNO_3Aq, but dissolved by HClAq, H_2SO_4Aq, KOHAq, and NaOHAq. Most specimens of Al contain Fe and Si; they are more easily oxidised than the pure metal.

Aluminium forms one series of salts the simplest formulæ of which represent them as derived from acids by replacement of H_3 by Al; *e.g.* $Al_2.3SO_4$, $Al3NO_3$ &c.

The atom of Al is trivalent in the gaseous molecule $AlCl_3$. Many experiments have been conducted to determine the mol. w. of Al chloride; Nilson a. Pettersson have finally shown (*Z. P. C.* 4, 206) that the only molecules which exist throughout a considerable range of temperature have the composition $AlCl_3$. Odling (*P. M.* [4] 29, 316) stated the V.D. of Al methide to be 36·2 at temperatures above 200° (and 72·4 at 130°); and hence mol. w. $Al(CH_3)_3$. It remained, however, uncertain whether the gas was homogeneous or not (*v.* Wanklyn, *P. M.* [4] 29, 313; Williamson, *ibid.* 395; Le Roux a. Louïse, *C. R.* 106, 73). Quincke (*Z. P. C.* 3, 164) has shown that the molecular formula of Al methide is $Al(CH_3)_3$.

The atomic weight of Al has been determined; (i.) by analyses and determination of V.D. of Al_2Cl_6, Al_2Br_6, and Al_2I_6; (ii.) by measurements of S.H. of Al; (iii.) by comparison of various compounds (*e.g.* Al_2O_3, and alum) with isomorphous compounds of Cr and Fe; (iv.) by analyses of ammonia-alum and Al_2Br_6, and by measuring the H evolved by the action of Al on NaOHAq (Mallet, *T.* 171, 1003 i.; *v.* also for older determinations Berzelius, *P.* 8, 187; Dumas, *A.Ch.* [3] 55, 151; Tissier, *C.R.* 46, 1105; Terreill, *Bl.* 31, 153).

Aluminium is a distinctly metallic element; no allotropic forms of it are known. According to the investigations of Wheatstone (*J.* 1855. 22), in KOHAq Al is electropositive to Cd, Sn, Pb, Fe, Cu, and Pt, and negative to Zn; in HClAq Al is positive to Sn and Pb, and negative to Zn and Cd. Al decomposes H_2O at 100°. It reacts with acids to form definite salts, but at the same time hydrated Al_2O_3 dissolves in alkalis to form unstable salts in which the Al forms a part of the negative, or acid, radicle (*v.* ALUMINATES).

The thermal value of the action of acids on $Al_2O_3.3H_2O$ is a large positive number approximately equal to the value for CdO_2H_2 and FeO_2H_2, although considerably less than the values of the corresponding actions with CaO_2H_2, SrO_2H_2, and BaO_2H_2 thus (Thomsen):—

M	[M, 2HCl Aq]	M	[M, 2HCl Aq.]
CaO_2H_2	30,490	$\frac{Al_2O_6H_6}{3}$	18,640
SrO_2H_2	27,630	CdO_2H_2	20,290
BaO_2H_2	40,012	FeO_2H_2	21,390

The difference between the heat of formation of a metallic chloride and hydroxide has usually a positive value; in the case of a non-metallic chloride and oxide the difference is usually a negative quantity (Thomsen, *Th.* 3, 531); in the case of Al the difference in question has a large negative value, thus $[Al^2, Cl^6] - [Al^2, O^3, 3H^2O] = -22,320$. Al shows several analogies with Be; they both very readily form basic and double salts; Al_2O_3 is less basic than BeO; both metals readily alloy with Si; neither seems to be easily acted on by S. For fuller discussion of the chemical relations of Al *v.* EARTHS, METALS OF THE.

Reactions.—1. Pure Al is unacted on by *ordinary air;* impure specimens of the metal become covered with a film of oxide.—2. *Water* is decomposed by Al at 100° with evolution of H.—3. *Con.* or dilute *nitric acid* has no action on Al.—4. The metal is easily dissolved by *hydrochloric acid.*—5. Dilute *sulphuric acid* evolves H, forming $Al_2.3SO_4$; hot *con.* H_2SO_4 evolves SO_2.—6. Most *carbon acids, e.g.* acetic, tartaric, have little or no action on Al; but in presence of NaClAq the action becomes marked, Al_2Cl_6 being formed.—7. *Sulphuretted hydrogen* has no action even at high temperatures.—8 *Aqueous potash or soda* dissolves Al, evolving H, and forming an aluminate (*v.* Cavazzi, *G.* 15, 202); molten KOH or NaOH does not act on Al.—9. *Sulphates, carbonates, borates, and silicates, of the alkali metals* are decomposed by Al at high temperatures.—10. *Potassium nitrate* oxidises Al when the two react at a white heat. 11. *Alkali sulphides* are without action even at high temperatures; *silver sulphide* when

heated with Al is partly reduced with formation of a Ag-Al alloy.—12. Many *metallic oxides* are deoxidised by Al at high temperatures, *e.g.* oxides of Pb, Cu, Fe; oxides of Zn and Mn are not acted on.—13. *Alkaline*, but not neutral or slightly acid, *solutions of lead, silver, and tin*, are reduced by Al with ppn. of the metals; Cu is ppd. from $CuSO_4Aq$.—14. Most *metallic chlorides* in solution are reduced by Al (KClAq, NaClAq are exceptions; Cossa, *Z.* [2] 6, 380, 443). Fused zinc chloride, but not $MgCl_2$, is reduced by Al (Flavitsky, *B.* 6, 195).

Combinations.—1. With *oxygen* to form Al_2O_3; only at high temperatures, and then superficially.—2. With *sulphur* to form an unstable compound (*v.* ALUMINIUM, SULPHIDE OF) only at very high temperatures.—3. Wöhler (*P.* 11, 160) states that Al combines with *phosphorus, selenion, tellurium, and arsenic*, when heated in the vapours of these elements; but little is known of the compounds.—4. With *boron* Al forms at least two compounds (*v.* ALUMINIUM, BORIDES OF).—5. With *chlorine, bromine*, and *iodine*, Al combines to form Al_2Cl_6, Al_2Br_6, and Al_2I_6 (*q.v.*).—6. Al forms *alloys* with most of the metals; these alloys are usually formed by heating the metals together; or sometimes by heating Al_2O_3 and carbon with the other metal. The properties of many metals are considerably changed by alloying with small quantities of Al. The alloys of Al with Cu, Ag, and Sn are much used because of their colour, hardness, and stability, and the ease with which they are worked. The alloys of Al have been chiefly studied by Calvert a. Johnson (*P. M.* [4] 10, 240); Tissier (*C. R.* 43, 885; 49, 54); Debray (*C. R.* 44, 925); Wöhler (*A.* 106, 118; 113, 248; 138, 253; *P.* 11, 161); Michel (*A.* 115, 102). The alloys with *copper* containing from 6 to 10 per cent. Al are yellow, hard, unacted on by moist air, water, or salt solutions, and are easily worked. The alloys with *silver* are also very stable, have a fine colour and may be highly polished. When a little Al is alloyed with *tin* the products are very hard and elastic. (These alloys will be more fully described under COPPER, SILVER, and TIN.) Alloys of Al with the following metals have been prepared:—Bi (a very little Bi makes Al extremely brittle); Ca (by heating Al, Na, and much $CaCl_2$, Wöhler); Cu, Cr (by heating Al with $Cr_2Cl_6.KCl$, Wöhler); Au, Fe, Mg, Mn (by heating $MnCl_2$, KCl, NaCl, and Al); Hg (Caillетet, *C. R.* 44, 1250); Mo, Ni, Pt, Ag, Na (this alloy easily decomposes H_2O); Sn, Ti, W (by heating WO_3 with Al, cryolite, and KCl, and NaCl); and Zn.

Detection.—Many Al compounds are soluble in water; most are dissolved by HClAq. Strongly heated Al_2O_3 is nearly insoluble in acids; it, and also the insoluble Al-containing minerals, may be dissolved by fusion with $KHSO_4$ and treatment with water (H. Rose, *P.* 1, 275).

Estimation.—1. Usually as Al_2O_3: a fairly *con.* solution is ppd. by a small excess of NH_3Aq (if Mg salts are present a good deal of NH_4ClAq is added), the free NH_3 is removed by warming, the pp. is washed, thoroughly dried, and strongly heated for some time.—2. $Al_2O_6H_6$ may also be ppd. by $Na_2S_2O_3Aq$. This method is specially applicable in presence of Fe salts; the two metals are ppd. as hydrates, the pp. is dissolved in HClAq, the solution is nearly neutralised by Na_2CO_3Aq and diluted so that 50 c.c. do not contain more than ·1 gram Al_2O_3, a slight excess of $Na_2S_2O_3Aq$ is added, and after a little the liquid is boiled so long as SO_2 comes off, the pp. of $Al_2O_6H_6$ mixed with S is filtered hot, washed with hot water, and strongly heated until all S is burnt off;

$(Al_2Cl_6Aq + 3Na_2S_2O_3Aq + 3H_2O =$
$Al_2O_6H_6 + 6NaClAq + 3S + 3SO_2;$
$Fe_2Cl_6Aq + 2Na_2S_2O_3Aq =$
$Fe_2Cl_4Aq + 2NaClAq + Na_2S_4O_6Aq)$ (*v.* Chancel, *C. R.* 46, 987).—3. Al is also sometimes estimated as a basic acetate (*v.* Atkinson, *Fr.* 3, 329; also Schulze, *J. pr.* 47, 313); or as basic formate (Schulze, *C. C.* 1861. 3). For methods of separating Al from alkaline earths *v.* Deville, *A. Ch.* [3] 38, 5; from Co, Ni, and Zn *v.* Haidlen a. Fresenius, *A.* 43, 129; from iron *v.* Macivor, *C. N.* 29, 199; from iron and phosphoric acid *v.* Flight, *C. J.* [2] 13, 592; also Esilman, *C. N.* 28, 208; from chromium *v.* Dexter, *P.* 89,142.

Aluminium, Alloys of, *v.* ALUMINIUM; *Combinations*, No. 6.

Aluminium, Arsenide of. According to Wöhler (*P.* 11, 160) Al combines with As when the elements are heated together; the product is a grey metal-like mass, decomposed by water with evolution of AsH_3. No analyses are given.

Aluminium, Borides of. Al seems to form two definite compounds with boron, AlB_2 and AlB_{12}. They may be obtained by packing a rod of Al in amorphous B in a carbon crucible, placing this in a Hessian crucible with powdered charcoal between the crucibles, covering, and heating to redness for 1½ or 2 hours; B_2O_3 may be used in place of B (10 parts B_2O_3 to 8 parts Al). On cooling, the fused mass is treated with HClAq, whereby Al dissolves and crystals of the borides remain, which may be separated by hand (Hampe, *A.* 183, 75). Both borides were obtained by Wöhler and Deville and regarded by them as crystallised boron (*A.* 101, 113, and 347; 141, 268); the compositions represented by the formulæ AlB_2 and AlB_{12} are assigned by Hampe (*l. c.*). AlB_2 crystallises in thin, lustrous, pale copper-coloured, six sided, plates; unchanged by heating in air; slowly dissolved by hot *con.* HClAq and NaOHAq, easily soluble in warm HNO_3Aq. This compound may be prepared by the action of BCl_3 vapour on hot Al; or by heating $BF_3.KF$ with KCl, NaCl, and Al. AlB_{12} forms black, monoclinic crystals, transparent in very thin plates; harder than corundum, softer than diamond S.G. = 2·534. These crystals are unacted on by *con.* HClAq or KOHAq, and very slowly by hot *con.* H_2SO_4Aq; they are soluble in hot *con.* HNO_3Aq. They are oxidised by molten KOH and $PbCrO_4$; also by molten $KHSO_4$; but are not acted on by molten KNO_3. Heated with Pt an easily fusible alloy is formed.

Aluminium, Borocarbide of. $Al_3C_2B_{48}$. Originally obtained by Wöhler and Deville, and supposed to be crystallised boron; examined more fully by Hampe (*A.* 183, 90). Prepared by long-continued heating at a very high temperature of B_2O_3 and Al in a graphite crucible (for details, *v.* Hampe, *l.c.*). The compound crystallises in yellowish, sparkling, crystals of the dimetric system. S G. = 2·615; hardness between that of diamond and corundum. The crystals

are slowly dissolved by hot *con.* HNO_3Aq, but not by HClAq, H_2SO_4Aq, or KOHAq; they behave towards molten KOH, $PbCrO_4$, and $KHSO_4$ similarly to AlB_{12} (*q.v.*).

Aluminium, Bromide of. $AlBr_3$ or Al_2Br_6; not certain. [abt. 90°] (Weber, *P.* 103, 251). (263°·3) at 747 mm. (Mallet, *T.* 1880. 1003). S.G. 2·54. V.D. 266·8 (Deville a. Troost, *A. Ch.* [3] 58, 257). H.F. $[Al^2,Br^6] = 239,440$ (*Th.* 3, 240).

Formation.—By passing Br vapour over a heated mixture of alumina and charcoal.

Preparation.—By the action of Br on excess of powdered Al, and subsequent repeated distillation from Al, and finally in atmosphere of N. (Mallet, *l.c.*)

Properties.—White, lustrous, plates; fumes in air; melts to a mobile liquid; soluble in CS_2, alcohol, and water, in latter with production of much heat $[Al^2Br^6, Aq] = 170,600$ (*Th.* 3, 240).

Reactions and Combinations.—Aqueous solution on evaporation *in vacuo* yields crystals of $Al_2Br_6, 12H_2O$; this solution is decomposed on heating into $Al_2O_6H_6$ and HBr. Al_2Br_6 is decomposed into Al_2O_3 and HBr when heated in air; it combines with the bromides of the alkali metals to form double salts, *e.g.* $2KBr.Al_2Br_6$ (Weber, *P.* 103, 259); it absorbs NH_3, also H_2S, forming compounds which are decomposed by heat (Weber, *l.c.*).

Aluminium, Chloride of. $AlCl_3$. Mol. w. 133·13 (800°–1500°) (Nilson a. Pettersson, *Z. P. C.* 4, 206). V.D. 66·5 (N. a. P. *l.c.*). H.F. $[Al,Cl^3] = 160,980$ (*Th.* 3, 240).

Formation.—1. By heating powdered Al to redness in dry Cl.—2. By passing HCl mixed with CS_2 vapour over crude alumina or clay heated to redness; Al_2S_3 is formed but is at once decomposed by the HCl (Curie, *C. N.* 28, 307).—3. By heating Al with various metallic chlorides, *e.g.* $ZnCl_2$ (Flavitsky, *B.* 6, 195).—4. By heating Al_2O_3 with NH_4Cl (Rose, *P.* 74, 569), or with PCl_5, BCl_3, or $SiCl_4$ (Troost a. Hautefeuille, *C.R.* 75, 1710 and 1819).

Preparation.—100 parts Al_2O_3 are made into a thick paste with 40 parts carbon by the help of starch paste, or oil; the paste is kneaded to a cylinder, which is dried, heated in a covered crucible, and removed while hot to a porcelain tube connected with a Cl apparatus; as soon as the apparatus is full of Cl, the cylinder is heated to redness; Al_2Cl_6 distils over into a receiver. It is purified by sublimation from Al in a closed tube bent to an obtuse angle.

Properties.—Transparent, deliquescent, hexagonal plates; colourless when pure, but usually yellowish because of presence of chlorides of Fe, S, &c. Fusible in large masses but volatilises without fusion if heated in small quantities. Soluble in water with production of much heat $[Al^2Cl^6, Aq] = 153,690$ (*Th.* 3, 240); soluble in alcohol, and ether; insoluble in benzene; unacted on by HClAq.

Reactions.—1. Fumes in *moist air* absorbing H_2O and giving off HCl.—2. Easily decomposed (to Al_2O_3 and HCl) by *steam* (Kuhnheim, *J.* 1861. 149).—3. Partly decomposed by *oxygen* at a red heat with evolution of Cl (Berthelot, *C. R.* 86, 787).—4. Heated to redness with *lime*, corundum (Al_2O_3) is formed; with *magnesia*, spinelle (Al_2O_4Mg) is produced (Daubree, *C. R.* 39, 135).—5. Decomposed below red heat by *potassium or sodium*, with production of Al, and KCl, or NaCl.—6. Molten Al_2Cl_6 is *electrolysed* to Al and Cl (Buff, *A.* 110, 257).—7. *Sulphuric anhydride* forms $Al_2.3SO_4$, SO_2, and Cl.—8. *Solution in water* is decomposed by *heat* into Al_2O_3 and HCl.

Combinations.—1. Dissolves in *water*; solution when slowly evaporated gives deliquescent crystals of $Al_2Cl_6.12H_2O$ (Bonsdorff, *P.* 27, 279).—2. Absorbs dry *ammonia* to form yellow $Al_2Cl_6.6NH_3$; when this is heated in a stream of dry H, $Al_2Cl_6.2NH_3$ is obtained (Persoz, *A. Ch.* 44, 319).—3. Combines with *phosphoretted hydrogen* to form a yellow powder $3Al_2Cl_6.2PH_3$, decomposed by H_2O giving off PH_3 (Rose, *P.* 24, 295).—4. *Phosphoric chloride* at 180° forms $Al_2Cl_6.2PCl_5$; crystalline, easily fusible, easily decomposed by H_2O (Weber, *P.* 107, 375).—5. Combines with some other *non-metallic chlorides*; chief combinations are $Al_2Cl_6.2POCl_3$ (Casselmann, *A.* 98, 220); $Al_2Cl_6.2NaCl$ (Weber, *P.* 118, 471); $Al_2Cl_6.SCl_4$, $Al_2Cl_6.SeCl_4$, and $Al_2Cl_6.TeCl_4$ (Weber, *P.* 104, 421). Forms a compound with H_2S which is decomposed by H_2O (Wöhler, *P.* 11, 160).—6. Combines with *chlorides of alkali metals* to form $Al_2Cl_6.2MCl$ (Degen, *A.* 18, 332; Deville, *A. Ch.* [3] 43, 30); the most important is $Al_2Cl_6.2NaCl$, white crystals, melting at about 185°, volatile at a red heat without decomposition; deliquescent, but much less so than Al_2Cl_6. This salt is prepared on the large scale, as from it the metal Al is obtained (*v.* ALUMINIUM, *Preparation of*).—7. By evaporating solutions of the mixed chlorides the compounds $Al_2Cl_6.2PdCl_2.20H_2O$ and $Al_2Cl_6.2PtCl_4.30H_2O$ were obtained (Welkow, *B.* 7, 304 and 802).—8. With *sulphurous anhydride* forms $Al_2Cl_6.2SO_2$, a heavy liquid, solidifying at −10° (Andrianowsky, *Bl.* [2] 31, 495).

Aluminium, Fluoride of. AlF_3. Mol. w. uncertain, as V.D. not determined. S.G. 3·1.

Occurrence.—In combination with NaF as *cryolite* $Al_2F_6.6NaF$; also with silicates in topaz, &c.

Formation.—1. By action of HF on Al_2O_3.—2. By fusing cryolite with $Al_2.3SO_4$, and digesting in water whereby Na_2SO_4 is dissolved and Al_2F_6 remains (Deville, *C.R.* 42, 49).

Preparation.—A mixture of fluorspar and alumina, in a boat of graphite, is heated to fusion in a tube of graphite, in dry HCl; crystals of Al_2F_6 sublime and $CaCl_2$ remains (Deville, *C. R.* 43, 971).

Properties and Reactions.—White, and very obtuse rhombohedra; unacted on by air, by acids, or by aqueous alkalis (Deville, *C. R.* 43, 970). Volatile at bright red heat.

Combinations.—1. With *hydrofluoric acid* and *water*: by dissolving Al_2O_3 in H_2SiF_6Aq, digesting with Al_2O_3 till SiO_2 is ppd. and solution is neutral, and evaporating, crystals of $Al_2F_6.7H_2O$ are obtained; if digestion with Al_2O_3 is stopped while liquid is distinctly acid but SiO_2 is ppd., and alcohol is added, $3Al_2F_6.4HF.10H_2O$ is formed; if, instead of adding alcohol, the acid liquid is evaporated $Al_2F_6.HF.5H_2O$ is produced (Deville, *A. Ch.* [3] 61, 327).—2. With *alkali fluorides* compounds of the form $Al_2F_6.6MF$ are formed, the most important of these are the K and the Na compounds. $Al_2F_6.6KF$ is obtained as a gelatinous pp. by adding a solution of Al_2O_3 in HFAq to an excess of KFAq. Al_2F_6.

$4KF$ is produced by adding $KFAq$ to excess of Al_2F_6 in $HFAq$; if the pp. is boiled in the liquid $Al_2F_6.6KF$ is formed. Both pps. form white powders when dry, and are decomposed with loss of all their F by heating with *con.* H_2SO_4Aq. $Al_2F_6.6NaF$ occurs native as cryolite on the west coast of Greenland. S.G. = 2·96. It may be prepared by the action of HFAq on Al_2O_3 and Na_2CO_3, mixed in ratio $Al_2O_3:3Na_2CO_3$, drying, and heating to fusion. Forms colourless, transparent, dimetric crystals; softer than felspar; melts below red heat, forming a colourless glass on cooling. Decomposed to CaF_2 and a solution of Al_2O_3 in NaOHAq, by boiling with milk of lime, or fusing with $CaCO_3$ and boiling in H_2O. Heated with H_2SO_4Aq loses HF, and produces $Al_2.3SO_4$ and Na_2SO_4.

Aluminium, Hydrated Oxide of, *v.* Aluminium, Hydroxides of.

Aluminium, Hydroxides of. Three compounds of Al, H, and O are known; they react rather as hydrated oxides, $Al_2O_3.xH_2O$ where $x = 1$, 2, and 3, than as hydroxides. Al_2O_3 which has not been strongly heated takes up H_2O; but the definite compounds are obtained by indirect methods; Al_2O_3 which has been strongly heated has no action on H_2O. The hydrates of Al_2O_3 lose their water at a red heat. When freshly ppd. they dissolve easily in acids, forming the same salts Al_2X_6 where X = acid radicle (*v.* Aluminium, Salts of). Thomsen gives the following thermal values $[Al^2, O^3, 3H^2O] = 388,920$; $[Al, O^3, H^3] = 297,000$; $\left[\frac{Al^2O^6H^6}{3}, H^2SO^4Aq\right] = 20,990$; $\left[\frac{Al^2O^6H^6}{3}, 2HClAq\right] = 18,640$ (*Th.* 3, 240). The hydrates also dissolve in KOHAq and NaOHAq with formation of easily decomposed aluminates (*q. v.*). The hydrates, especially $Al_2O_3.3H_2O$, form a class of bodies called *lakes* by their action on vegetable colouring matters; they pp. these colouring matters from solutions, hence these hydrates are used as *mordants*.

I. Monohydrate. $Al_2O_3.H_2O$ ($= Al_2O_4H_2$). Occurs native as *diaspore*, in transparent, trimetric crystals, S.G. 3·43, which crumble to powder when heated but lose all H_2O only at about 360°; insoluble in water and in boiling HClAq. By heating amorphous Al_2O_3 in a closed tube with H_2O to 240°–250° Mitscherlich obtained hydrated Al_2O_3 nearly agreeing in composition with formula $Al_2O_3.H_2O$ (*J. pr.* 83, 468). According to Becquerel (*J.* 1868. 87; *J.* 1874. 132) crystalline $Al_2O_3.H_2O$ is produced when a tube containing Cr_2Cl_6Aq and covered with parchment paper is suspended in a solution of Al_2O_3 in KOHAq.

II. Dihydrate. $Al_2O_3.2H_2O$ ($= Al_2O_5H_4$). Occurs native as amorphous *bauxite* (Berthier, *S.* 35, 154). Prepared by the action of NH_4ClAq on Al_2O_3 in KOHAq, washing, and drying at 100° (Löwe, *Z.* 3, 247); also by ppg. hot solutions of Al salts by NH_3Aq, digesting the pp. in the warm liquid, washing, and drying at 100° (St. Gilles, *A. Ch.* [3] 46, 58). A dihydrate is also obtained by the slow decomposition of basic aluminium acetate, and subsequent evaporation to dryness at 100° (*v.i.*). The dihydrate is said to be nearly insoluble in acids and aqueous alkalis. Two varieties of $Al_2O_3.2H_2O$ in aqueous solutions were obtained by Crum (*C. J.* 6, 225), and Graham (*T.* 1861. 183), respectively. Crum prepared basic Al acetate

$$(2Al_2(C_2H_3O_2)_6.Al_2O_6H_6.3H_2O),$$

dissolved this by heating with much water, heated this solution to 100° in a closed tube for ten days, whereby the salt was decomposed into acetic acid and $Al_2O_3.xH_2O$, then diluted, and boiled in an open vessel until all acetic acid was removed. The solution of $Al_2O_3.xH_2O$ thus obtained was colourless, tasteless, and neutral to litmus; it was easily coagulated by small quantities of sulphuric, citric, tartaric, and many other acids, and by various salts, not by acetic, formic, boric, and one or two other acids. This solution does not act as a mordant; evaporated at 100° $Al_2O_3.2H_2O$ insoluble in acids is oobtined; the coagulated hydrate dissolves in *con.* acids. Graham dissolved $Al_2O_3.xH_2O$ in Al_2Cl_6Aq or in Al acetate solution, and dialysed; the aqueous solution of $Al_2O_3.xH_2O$ thus obtained was very easily coagulated by acids, alkalis, and salts; it acted as a mordant; the coagulated hydrate dissolved easily in dilute acids.

III. Trihydrate. $Al_2O_3.3H_2O$ ($= Al_2O_6H_6$). Occurs native, in hexagonal, fibrous, crystals, as *gibbsite*, and *hydrargyllite*. Prepared by ppg. cold solution of Al salts by NH_3Aq, or $(NH_4)_2CO_3Aq$, washing, dissolving in HClAq, reppg., washing, and drying at 100°. A soft, friable, white powder; easily soluble in acids and fixed aqueous alkalis; insoluble in water. When freshly ppd. it forms a gelatinous mass, soluble to some extent in NH_3Aq, but reppd. on standing in air. Heated to redness it loses all its H_2O, and contracts considerably. A crystalline trihydrate is formed by the action of air on a saturated solution of Al_2O_3 in KOHAq (Bonsdorff, *P.* 27, 275); it is insoluble in cold acids, slowly dissolved by boiling HClAq, more rapidly by H_2SO_4Aq. $Al_2O_3.3H_2O$ is also said to be formed by the action of H_2O on Al amalgam (Cossa, *Z.* 13, 443).

Aluminium, Iodide of. AlI_3 or Al_2I_6; not certain. [abt. 185°] (abt. 360°) (Weber, *P.* 101, 465; 103, 259). S.G. 2·63. V.D. 387·4 (Deville a. Troost, *A. Ch.* [3] 58, 257). H.F. $[Al^2, I^6] = 140,780$ (*Th.* 3, 240).

Preparation.—Al in small pieces is placed in a retort, about ½ to 1 p.c. of the calculated quantity of I is added, CO_2 is led in, and the retort is heated until combination occurs; rather less than the quantity of I needed to convert all the Al into Al_2I_6 is then added, and heating, in a steam of CO_2, is continued until Al_2I_6 sublimes (Gustavson, *A.* 172, 173).

Properties, &c.—White, deliquescent, plates; soluble in alcohol, and CS_2; soluble in water with production of much heat $[Al^2I^6, Aq] = 178,000$ (*Th.* 3, 240). Solution in H_2O on standing over H_2SO_4 gives $Al_2I_6.12H_2O$. Decomposed by heating in O (Schulze, *J. pr.* [2] 21, 40). Forms double salts with alkali iodides; absorbs NH_3; apparently does not combine with H_2S (Weber, *P.* 101, 465; 103, 259).

Aluminium, Nitride of. Al heated in N increases in weight, and heated with molten NaOH evolves NH_3 (Briegleb a. Geuther, *A.* 123, 238). The compound Al_2N_2 was obtained by Mallet (*C. J.* [2] 15, 349) by heating Al with Na_2CO_3 to the highest temperature of a wind furnace for some hours in a graphite crucible,

and treating the residual mass with HClAq. The compound is pale-yellow when amorphous, bright honey-yellow and very lustrous when crystallised; brittle, not hard enough to scratch glass; in moist air it slowly crumbles down to Al_2O_3 with evolution of NH_3; it is dissolved by aqueous alkalis with evolution of NH_3 and solution of Al; fused with KOH or NaOH, an aluminate is formed and NH_3 is given off; heated in air, NH_3 is evolved and Al_2O_3 remains.

Aluminium, Oxide of. [There are some indications of the existence of an oxide containing more O than Al_2O_3 (*v.* Gibson a. Morrison *P.R.S.E.* 119, 146, 152).] Al_2O_3 (*Alumina*) Mol. w. unknown. S.G. (amorphous) 3·725 to 4·152 (Rose, *P.* 74, 429); (crystalline) 3·928. S.H. (corundum, 9°–98°) ·19762; (sapphire, 8°–97°) ·21733 (Regnault, *A. Ch.* [3] 1, 129).

Occurrence.—Native, nearly pure as *corundum, sapphire, topaz, amethyst,* &c.; also in opaque variety as *emery*.

Formation. — I. Amorphous. — 1. By burning powdered Al in oxygen.—2. By ppg. boiling solution of potash-alum by $(NH_4)_2CO_3Aq$, washing, and strongly heating.—3. By strongly heating ammonia-alum.—4. By digesting clays, felspathic rocks, &c., with *con.* KOHAq under pressure, and ppg. by CO_2.—5. By heating a mixture of cryolite and lime in steam, lixiviating, and ppg. by CO_2.—II. Crystalline.—1. By fusing the amorphous Al_2O_3 in the oxyhydrogen flame (Gaudin, *C. R.* 49, 1342).—2. By heating equal parts of potash alum and K_2SO_4 with charcoal (Gaudin, *A.* 103, 92).—3. By fusing together Al phosphate with three or four parts of K_2SO_4 or Na_2SO_4 (Debray, *C. R.* 52, 895).—4. Along with $Al_2O_3.H_2O$, by heating a solution of Al_2O_3 in HClAq to 350° in a closed tube (Sénarmont, *C. R.* 32, 762).—5. By heating to bright redness equal parts of amorphous Al_2O_3 and PbO (Deville a. Caron, *A. Ch.* [4] 5, 104).

Preparation.—The *amorphous* variety may be prepared by heating dry potash-alum for two or three hours to redness, finely powdering the residue, washing with water, mixing with NaOHAq containing $\frac{1}{10}$ as much NaOH as the potash-alum used, drying, strongly heating, and washing with water (Wöhler, *A.* 53, 422; Brunner, *P.* 98, 488). *Crystalline* Al_2O_3 may be prepared by heating to whiteness a mixture of one part amorphous Al_2O_3 with four parts fused borax (Ebelmen, *A. Ch.* [3] 33, 34). Large crystals 1 cm. long were obtained by Deville a. Caron (*A. Ch.* [4] 5, 104) by the action of Al_2F_6 on boric acid at a high temperature. The Al_2F_6 was placed in a graphite crucible, the boric acid being contained in a small Pt basin fixed above the Al_2F_6; the whole was placed in a Hessian crucible and heated in a wind furnace for some time; BF_3 was volatilised and crystals of Al_2O_3 remained.

Properties.—Known in two forms, amorphous and crystalline. The *amorphous* variety is a white, soft, powder; cakes together when strongly heated, and becomes nearly as hard as corundum; infusible except in oxyhydrogen blowpipe; insoluble in water; soluble in acids and aqueous alkalis, but after strongly heating becomes insoluble in acids except *con.* H_2SO_4Aq and *con.* HClAq. The *crystalline* variety forms colourless rhombohedra; insoluble in all acids; nearly as hard as diamond. Both forms are undecomposed by heat, and are unacted on by Cl.

Reactions.—1. With *acids* amorphous Al_2O_3 reacts to form Al salts—*e.g.* $Al_2.3SO_4$.—2. Fused with *potash* or NaOH, or $KHSO_4$, both amorphous and crystalline Al_2O_3 form aluminates (*q. v.*) which are soluble in water.—3. Amorphous Al_2O_3 heated to whiteness with *potassium* is partly deoxidised with formation of an alloy of K and Al. 4. Heated with *sal ammoniac*, Al_2Cl_6 is formed; the same compound is produced by the action of hot BCl_3, or $SiCl_4$.—5. Al_2S_3 is said to be formed by the action of *carbon disulphide* vapour on hot Al_2O_3.—6. *Water* is taken up by slightly heated amorphous Al_2O_3, but no definite hydrates have been thus obtained (*v.* ALUMINIUM, HYDROXIDES OF).

Aluminium, Oxychlorides of. A series of these compounds seems to exist; they may be obtained by the action of a mixture of Al_2Cl_6 vapour and O on Al; the higher the temperature the more O is there in the product; they are soluble in dilute acids and alkalis, and are decomposed by water (Hautefeuille a. Perrey, *C. R.* 100, 1219). Tommasi (*Bl.* [2] 37, 443), describes three compounds of $Al_2O_6H_6$ with Al_2Cl_6 obtained by the action of Al on $CuCl_2Aq$ under different conditions.

Aluminium, Phosphide of. Described by Wöhler (*P.* 11, 160) as a dark grey mass, which decomposes H_2O evolving PH_3; produced by heating powdered Al to redness in vapour of P.

Aluminium, Salts of. *Salts obtained by replacing H of acids by Al.* These salts belong to the form Al_2X_6, or AlX_3, where X = NO_3, $\frac{PO_4}{3}$, $\frac{CO_3}{2}$, $\frac{SO_4}{2}$ &c.; besides these, many basic salts (compounds of normal salts with $Al_2O_3.xH_2O$) are known. Very many Al salts also form double salts; the most characteristic of which are the alums $Al_2.3SO_4.M_2SO_4.24H_2O$, where M = an alkali metal, Ag, or Tl (*v.* ALUMS). The haloid salts, the normal nitrate, sulphate, and acetate, are soluble in water; most of the other normal salts, and almost all the basic salts, are insoluble in water. The soluble salts possess a sweetish, astringent taste. Aqueous solutions of Al salts generally contain more or less free acid, which is not, however, to be detected by the ordinary tests; Erlenmeyer a. Lewinstein (*Z.* 3, 572) add freshly ppd. $Mg.NH_4.PO_4$, which pps. $Al_2(PO_4)_2$, and forms $MgSO_4$ and $(NH_4)_2SO_4$, the acid can then be detected by litmus &c. The number of Al salts is not very large; with some acids, *e.g.* sulphurous carbonic, &c., it forms no salts or very unstable ones which can hardly be obtained pure. The chief salts—described under BORATES, PHOSPHATES, &c.—are the *borates, nitrates, phosphates, silicates,* and *sulphates*: *v.* also CARBONATES, SULPHITES, SELENATES, &c.

Aluminium, Selenide of. According to Wöhler, Al when heated in Se vapour combines with the latter to form a black powder which is decomposed by H_2O into $Al_2O_3.xH_2O$ and H_2Se (*P.* 11, 160).

Aluminium, Silicides of. Al and Si react in almost all proportions; the products seem to be of the nature of alloys. When Al is heated with silicates in presence of a flux,

portion of the silica is reduced and combines with part of the Al. An alloy containing 10·3 p.c. Si, called *cast aluminium*, is grey and very brittle; an alloy with 70 p.c. Si still exhibits metallic properties. The alloys of Si and Al are much more easily acted on by reagents than either of the elements which form them.

Aluminium, Sulphide of. Al_2S_3.

If Al is heated to glowing and S is then thrown on to it, a black mass is produced which is decomposed by H_2O with evolution of H_2S. A mixture of Al_2S_3 and Al_2O_3 is obtained by passing CS_2 vapour over red-hot Al_2O_3. When $Al_2.3SO_4$ is heated in H, Al_2O_3 remains and H_2SO_4 is volatilised (Wöhler, *P.* 11, 160). The best method of preparing Al_2S_3 seems to be to pass S vapour over hot Al in a carbon boat placed in a porcelain tube kept full of H. It is described as yellow crystals, with a bitter taste, which melt with difficulty, and are rapidly acted on by water with formation of H_2S and $Al_2O_3.xH_2O$ (Fremy, *A. Ch.* [3] 38, 322; Sabatier, *A. Ch.* [5] 22, 88; Reichel, *J. pr.* [2] 12, 55). Spring (*Bl.* [2] 39, 64) obtained a sulphide of Al by very strongly compressing an intimate mixture of Al and S.

Aluminium, Telluride of. Described by Wöhler as a black powder produced by heating together Al and Te (*P.* 11, 160).

M. M. P. M.

ALUMINIUM AMYLATE *v.* AMYL ALCOHOL.

ALUMINIUM BROMIDE, Action of, on Organic Bodies.—Aluminium bromide assists the bromination of aromatic hydrocarbons. The action appears to be preceded by the formation of a compound $AlBr_36C_nH_{2n-6}$ (Gustavson, *J.* 1877, 400; 1878, 380; *B.* 18, Ref. 208). $AlBr_3$ also combines with butylene; thus, when HBr mixed with C_2H_4 is passed into $AlBr_3$ at 60°, the compound $AlBr_3C_4H_8$ is formed; the same compound is formed from $AlBr_3$ and C_2H_5Br, and by passing HBr into American or Caucasian petroleum containing $AlBr_3$ at 70° (Gustavson, *J. R.* 16, 95; *B.* 17, Ref. 163).

The compound $AlBr_3C_4H_8$ is an oil, insol. in light petroleum or CS_2; it is decomposed by water with formation of unsaturated hydrocarbons and by alkyl bromides at 70° with formation of paraffins (Gustavson, *J. pr.* [2] 34, 161).

Aluminium bromide converts alkyl chlorides into bromides.

ALUMINIUM ISO-BUTYL $C_{12}H_{27}Al$ *i.e.* $Al(C_4H_9)_3$. From Al and $Hg(C_4H_9)_2$. Fuming liquid (Cahours, *J.*, 1873, 522).

ALUMINIUM ISO-BUTYLATE *v. iso*-BUTYL ALCOHOL.

ALUMINIUM CHLORIDE, Action on Organic Bodies.—Aluminium chloride is converted by C_2H_4 and HCl at 100° into the compound $AlCl_3C_4H_8$ (G.).

Aluminium chloride added to a mixture of an aromatic hydrocarbon and an alkyl or alkoyl chloride, bromide or iodide, promotes the evolution of HCl, HBr, or HI and is therefore a most powerful agent in organic synthesis as a means of introducing alkyl or alkoyl groups into an aromatic nucleus (Friedel a. Crafts, *C. R.* 84, 1392, 1450; 85, 74, 672; 86, 1368). Thus methyl-benzenes may be formed by this means from benzene and methyl chloride; acetophenone from benzene and acetyl chloride. The operation is performed by dissolving the aromatic hydrocarbon and the haloid derivative in CS_2 or light petroleum, and adding $AlCl_3$ in successive small portions. The reaction is completed by heating on a water-bath. Condensation is also brought about by $AlCl_3$ by the removal of water; thus benzene and Ac_2O form acetophenone; while benzene and phthalic anhydride form benzoyl-benzoic acid. Under the influence of $AlCl_3$ other reactions also occur; thus benzene is converted by oxygen, sulphur, sulphurous acid, and carbonic acid into phenol, phenyl-mercaptan, benzene sulphinic acid, and benzoic acid, respectively.

These reactions are perhaps due to the formation of such compounds as $AlCl_33C_6H_6$ in which the benzene may be supposed to be more unstable than when in the free state; thus, we might imagine the compound to be $AlH_3Cl_3Ph_3$. Molecular changes may, however, take place in the alkyls; thus both *n*- and *iso*-propyl bromides are converted by $AlBr_3$ into the same isopropyl-benzene; this is because *n*- propyl bromide is changed by $AlBr_3$, into its isomeride (Gustavson, *J.* 1878, 380; *P.* 16, 958).

In the above cases $AlCl_3$ induces the building up of more complicated compounds, but this reaction may be reversed and alkyl groups removed instead of introduced. Thus ethylbenzene, heated with $AlCl_3$ in a stream of HCl, evolves ethyl chloride and is reduced to benzene (Jacobsen, *B.* 18, 338). When the alkyl chloride is not carried off by a stream of HCl it may act by substitution upon another portion of the hydrocarbon. Thus toluene is converted by boiling with $AlCl_3$ into benzene and xylene (Anschütz a. Immendorff, *B.* 17, 2816). Somewhat similar reductions occur in other cases, the hydrogen being derived from another portion of the hydrocarbon. Thus naphthalene gives naphthalene dihydride, by reduction, and iso-dinaphthyl, by abstraction of hydrogen; benzene gives toluene and ethyl-benzene together with di-tolyl; di-phenyl-methane is reduced to benzene and toluene (Friedel a. Crafts, *B. A.* 1884, 468; *C. R.* 100, 692).

$AlCl_3$ acting upon *n*-propyl iodide gives propylene and HI, which then react, producing propane (Köhnlein, *B.* 16, 560). Aluminium bromide or iodide acting on propyl chloride or iodide at 130° form propylene but no propane (Kerez, *A.* 231, 286). $AlCl_3$ acting upon alcohols and phenols eliminates HCl; thus phenol gives $(PhO)_3Al_2Cl_3$; resorcin gives $(C_6H_4O_2)Al_2Cl_4$; and di-chlorhydrin gives $C_3H_5Cl_2O.AlCl_2$, which crystallises from CS_2. These compounds are at once decomposed by water into the alcohol, $Al(OH)_3$, and HCl (Claus a. Mercklin, *B.* 18, 2932). Acetyl chloride in CS_2 is converted by $AlCl_3$ into a white solid, $C_{12}H_{14}O_6Al_2Cl_8$, whence water produces a liquid $C_5H_8O_2$ (137°) which may be acetyl-acetone (Combes, *C. R.* 103, 814).

ALUMINIUM ETHIDE AlC_6H_{15} *i.e.* $AlEt_3$ (194°). V.D. 4·5 (for 3·9) at 234°. From mercuric ethide and aluminium heated at 100° for some hours (Buckton a. Odling, *Pr.* 14, 20). Liquid; fumes violently in air, soon taking fire. Decomposed by water. *Iodine* forms EtI.

Aluminium iodo-ethide $Al_2C_6H_{15}I_3$ *i.e.* $Al_2Et_3I_3$, (340°–350°), is a fuming liquid formed

by action of EtI on Al at 130° (Cahours, *A. Ch.* [3] 58, 5; *A.* 114, 242).

ALUMINIUM ETHYLATE *v.* ALCOHOL.

ALUMINIUM IODIDE, Action on Organic Bodies. AlI_3 turns out Cl displacing it by I, *e.g.* $3CCl_4 + 4AlI_3 = 3CI_4 + 4AlCl_3$ (Gustavson, *A.* 172, 173). Aluminium iodide and aluminium are singly without action on alcohol, but together they react, forming $Al_2I_3(OEt)_3$ and $Al_2(OEt)_6$. One molecule of aluminium iodide may convert very many molecules of aluminium into aluminium ethylate (*v.* ALCOHOL). Other alcohols act similarly (*v.* PROPYL, BUTYL, and AMYL, ALCOHOLS, CRESOL, PHENOL, NAPHTHOL THYMOL), but methyl and iso-propyl alcohols, glycol, and glycerin do not; the latter forms allyl alcohol (Gladstone a. Tribe, *Pr.* 30, 546, *C. J.* 39, 2; 41, 5; 49, 25; Hodgkinson, *C. N.* 1877, 237). Aluminium behaves in a similar way towards water and ether; it does not attack these bodies until after iodine has been added, when it reacts with water thus: $3H_2O + Al = Al(OH)_3 + H_3$, with which may be compared its action on alcohol: $3HOEt + Al = Al(OEt)_3 + H_3$, while with ether it forms aluminium iodo-ethylate and EtI.

ALUMINIUM METHIDE AlC_3H_9 *i.e.* $AlMe_3$ [c. 0°]. (130°). V.D. 2·8 (for 2·5) at 220°; 4 at 160°. From $HgMe_2$ and Al at 100° (Buckton a. Odling, *Pr.* 14, 19). Takes fire in air. Resembles $AlEt_3$. Just above its boiling-point the compound seems to be Al_2Me_6.

ALUMINIUM PROPYL
AlC_9H_{21} *i.e.* $Al(C_3H_7)_3$. (240°–245°).
From $HgPr_2$ and Al (Cahours, *J.* 1873, 518).

ALUMS.—*Double sulphates or selenates having the composition expressed by the general formula* $M_2 3S(or Se)O_4 . N_2S(or Se)O_4 . 24H_2O$, *where M = Al, Cr, Mn, Fe, In, or Ga; and N = Na, K, Rb, Cs, NH₄, Ag, or Tl.* These salts crystallise in forms belonging to the regular system, usually in octahedra or cubes. The following are the best-known alums:—I. SULPHATES: (1) M = Al, and N = Na, K, Rb, Cs, NH_4, $NH_3(C_2H_5)$, Ag, or Tl; (2) M = Cr, and N = Na, K, or NH_4; (3) M = Mn, and N = K, or NH_4; (4) M = Fe, and N = K, or NH_4; (5) M = Ga or In, and N = NH_4; (6) M = CrAl, and N = K, or NH_4. II. SELENATES: (1) M = Al, and N = Na, K, or NH_4; (2) M = Cr, and N = K, or NH_4. III. MIXED SELENATES AND SULPHATES, $M_2 3SeO_4 . N_2SO_4 . 24H_2O$: (1) M = Al, and N = K; (2) M = Cr, and N = K; (3) M = Fe, and N = K. IV. MIXED SULPHATES AND SELENATES, $M_2 3SO_4 . N_2SeO_4 . 24H_2O$: (1) M = Al, and N = K; (2) M = Cr, and N = K; (3) M = Mn, and N = K; (4) M = Fe, and N = K. Besides these, there are certain double salts which resemble, but are not isomorphous with, the alums; of these **pseudo-alums** the most important are the following:—I. Compounds of $Al_2 3SO_4$ with (1) $MnSO_4$, (2) $FeSO_4$, (3) $MgSO_4$; each with $24H_2O$. II. Compounds of $Fe_2 . 3SO_4$ with (1) $MgSO_4$, (2) $CuSO_4$, (3) $ZnSO_4$; each with $24H_2O$. III. $Mn_2 3SO_4 . MgSO_4 . 24H_2O$.

In naming the alums, if no prefix is used, a double sulphate of aluminium and one of the metals represented by N in the formula is understood; thus potassium alum is

$$Al_2 3SO_4 . K_2SO_4 . 24H_2O.$$

The sulphates containing no aluminium are spoken of as chromium-sodium alum, iron-ammonium alum, &c. Similarly, the names ammonium selenio-alum, and chromium-potassium selenio-alum are used for the members of Group II. The salts belonging to Groups III. and IV. may be called selenio-sulphuric alums; the individual bodies are best distinguished by their formulæ.

The alums are all soluble in water, their solubility in hot, being considerably greater than in cold, water; (potash alum, S. 3·29 at 0°; S. 22 at 30°; S. 31 at 60°; S. 357 at 100°). The solutions have a styptic taste and an acid reaction. Some of the alums are separated by water into their constituent salts, *e.g.* silver alum, and manganese-ammonium and potassium alums. Others are partially separated; indeed it appears very probable that every alum is to some extent separated into its constituents when dissolved in a considerable quantity of water. Thus, Favre and Valson (*C. R.* 74, 1165) find the heats of solution of one equivalent of aluminium sulphate (1) in water, (2) in a solution of K_2SO_4, and (3) in a solution of $(NH_4)_2SO_4$, to be the same (about −8,000); hence no combination occurs between the two sulphates in the presence of water. Further the heats of solution in water of the alums have large negative values, and in some cases—*e.g.* iron-ammonium alum—this value increases considerably as temperature rises (Favre and Valson, *C. R.* 74, 1016). G. Wiedemann (*P.* 126, 1; 135, 177), by determining the *specific magnetism* (that is, magnetic moment developed by unit magnetising force ÷ mass of salt in unit volume) of various salts in solution, has shown that an aqueous solution of ferric sulphate is partly separated into sulphuric acid and colloidal ferric oxide, and that the amount of this separation increases the larger the quantity of water added; he has also shown that an aqueous solution of iron-ammonium alum behaves almost exactly in the same way as ferric sulphate; hence the separation of the ferric sulphate by the water is independent of the alkaline sulphate; and hence a dilute aqueous solution of this alum is to a large extent separated into its constituent salts. When an aqueous solution of potassium alum saturated at 12° is heated to 100° a precipitate is slowly formed containing varying quantities of Al_2O_3, K_2O, SO_3, and H_2O; even after 30 days the precipitate continues to be produced. The decomposition of the alum is hastened by adding K_2SO_4 to the solution (A. Naumann, *B.* 8, 1630). Chromium-potassium alum exists in two forms; as violet crystals, and as a green non-crystallisable salt. When a solution of the former salt in water is heated to 70°–80° the colour changes to green, and this change is attended with a gradual increase of the volume of the solution; as the green solution cools the colour slowly changes to violet-blue, and the volume of the liquid slowly decreases (Boisbaudran, *C. R.* 79, 1491). The violet crystals change at 300°–350° to the green salt with loss of all their water of crystallisation; this green dehydrated alum is wholly soluble in hot water, but when heated somewhat above 350° it suddenly changes to greenish-yellow and becomes quite insoluble in water (Lowel, *A. Ch.* [3] 44, 313; Siewert, *A.* 126, 86). When a quantity of barium chloride sufficient to precipitate all the acid in a given

mass of chromium-potassium alum is added in four equal portions to an aqueous solution of the green form of this alum, the first and second fourths of the barium are at once precipitated, but the rest only very slowly; moreover, the quantity of heat produced during the precipitation of the first and second fourths is much greater than that produced during the subsequent precipitations (Favre and Valson, *C. R.* 74, 1165). Thus,

Gram-units of heat produced.

Excess of $BaCl_2$.	1st fourth.	2nd fourth.	3rd & 4th fourths.
8251	4104	4102	146

These results taken together show that solution in water of the commoner (probably of all) alums is accompanied by partial separation of these compounds into their constituent salts, and also by partial decomposition of these constituents, certainly at least of the sulphate of the heavy metal; and that the amount of this separation and decomposition is increased by increasing the quantity of water, or by raising the temperature.

The alums are dehydrated by the action of heat; at a higher temperature a portion of the acid radicle is usually volatilised, and a double basic sulphate remains, such as native alum stone $Al_23SO_4.K_2SO_4.2Al_2O_3.8H_2O$; at a still higher temperature more acid is removed and a mixture of alkaline sulphate and oxide of Al, Cr, Mn, or Fe remains; the ammonium alums leave a residue of oxide only. For descriptions of the properties of the individual alums *v.* SULPHATES.

M. M. P. M.

DI-ALURIC ACID *v.* DIALURIC ACID.

AMALGAMS. *Alloys of Mercury* (*v.* ALLOYS). Amalgams are formed (1) by direct union of mercury with other metals; *e.g.* amalgams of alkali metals, of Zn, Pb, Sn, Au: (2) by precipitation of other metals from solutions of their salts on mercury; this is often done by placing sodium-amalgam in the solution of a metallic salt, sometimes by electrolysing a metallic solution in presence of mercury; *e.g.* amalgams of Ag, Fe, Co, Ni, Mn, Ba: (3) by precipitation of mercury on another metal, sometimes it is necessary to electrolyse the mercurial solution, making the other metal one of the electrodes; *e.g.* amalgams of Cu, Ag, Au, Pt: (4) by placing the other metal in contact with mercury and a dilute acid; *e.g.* Zn amalgam. The formation of amalgams is not usually attended with any marked thermal change, but in the production of amalgams of the alkali metals much heat is produced. Thus, $[Na,Hg]=10,300$; $[Na,Hg^6]=21,600$; $[K,Hg^{\frac{1}{2}}]=20,300$; $[K,Hg^{12}]=34,200$ (Berthelot, *C. R.* 88, 1110, 1335). In the formation of amalgams of Sn, Pb, and Bi, heat is absorbed. Little or no contraction of volume accompanies the formation of amalgams, except in the cases of Cu, Ag, Sn, Pb, and a few other metals. The relative conductivity for heat of some solid amalgams is considerably greater than that of either of the metals composing them; *e.g.* amalgams of Sn, Zn, and Bi. Many solid amalgams seem to be chemical compounds in definite proportions; thus when various amalgams containing excess of mercury were subjected to a pressure of about 70 tons on the square inch mercury was removed, and definite bodies remained, containing mercury and metal approximately in the ratios expressed by the formulæ CuHg, AgHg, FeHg, Zn_2Hg, Pb_2Hg, PtHg, (Joule, *C. J.* 16, 378). Again, when amalgams of Au, Ag, Cu, Pb, K, and Na, were heated near to, to, or above, the boiling-point of mercury (360°), the following definite amalgams were obtained (De Souza, *B.* 8, 1616; 9, 1050):—

At 310° Au_8Hg $Ag_?Hg$ $Cu_{14}Hg$
„ 360° Au_8Hg $Ag_{11}Hg$ $Cu_{14}Hg$ Pb_8Hg
„ 440° Au_9Hg $Ag_{13}Hg$ $Cu_{16}Hg$ K_2Hg Na_3Hg.

Some of the liquid amalgams may be regarded as solutions of definite compounds in excess of mercury, *e.g.* liquid Na and K amalgams; others as solutions of metals in mercury, *e.g.* some of the iron amalgams. For descriptions of individual amalgams see the articles on the different metals, also MERCURY. M. M. P. M.

AMALGAMATION. The process of forming *Amalgams, q. v.*

AMALIC ACID $C_{12}H_{14}N_4O_8$ *i.e.* $C_8H_2Me_4N_4O_8$. *Tetra-methyl-alloxantin.*

Formation.—1. On mixing a solution of di-methyl-alloxan with one of di-methyl-dialuric acid, amalic acid is ppd. (Maly a. Andreasch, *M.* 3, 103).—2. A product in the oxidation of caffeïne by chlorine or nitric acid (Rochleder, *A.* 71, 1).—3. By reducing di-methyl-alloxan by H_2S (E. Fischer, *B.* 14, 1912).

Properties.—Transparent colourless crystals. Stains the skin red. V. sl. sol. cold water or alcohol, sl. sol. hot water. Reduces silver salts. It forms deep violet compounds with baryta, KOH, or NaOH.

Reactions.—1. Oxidised by *nitric acid* to di-methyl-alloxan, or, better, by passing *chlorine* into water in which it is suspended.—2. Amalic acid may be *distilled* without leaving a residue, but it is decomposed and in the distillate there is a crystalline acid, $C_{12}H_{14}N_4O_6$, '*desoxyamalic*' acid [260°]. This acid is v. sol. chloroform or glacial acetic acid, sparingly so in cold alcohol, water or ether. Soluble in alkalis but reppd. by HCl. Is partly decomposed when distilled. Reduces boiling ammoniacal $AgNO_3$. Evaporated with HNO_3 it forms dimethyl-alloxan. Chromic mixture converts it into cholestrophane. Hence it is possibly (Fischer a. Reese, *A.* 221, 339):

```
MeN – CO      CO.NMe
 |     |       |   |
 CO   HC   –  CH  CO
 |     |       |   |
MeN – CO      CO.NMe
```

3. *Hydrogen sulphide* forms di-methyl-dialuric acid (M. a. A.).—4. By *boiling with water* in an open vessel di-methyl-oxamide is produced:

$$C_{12}H_{14}N_4O_8 + H_2O + O_2 = 2C_4H_8N_2O_2 + 4CO_2.$$

5. *Ammonia gas* turns it violet, forming *murexoïn*, a crystalline body resembling murexide.—6. From the solution made by heating amalic acid (4 pts.) with *cyanamide* (2 pts.) and water (100 pts.) there separates out, on cooling, crystalline *cyamido-amalic acid* $C_{13}H_{14}N_6O_7$. Long prisms, sl. sol. cold water, v. sol. hot water, insol. alcohol or ether; reduces silver salts, and yields methylamine and an oxalate when boiled with alkalis. It gives off purple vapours when heated, and forms a sublimate (Andreasch, *M.* 3, 433).

AMANITINE *v.* NEURINE.

AMARINE *v.* BENZOIC ALDEHYDE.

AMBER. A fossil resin from *Pinites succinifer*. S.G. 1·05 to 1·10. It contains from 3 to 8 p.c. succinic acid, also a resin [146°] soluble in ether but not in alcohol, a resin [105°] soluble in alcohol and other bodies. There is about 1 p.c. ash (O. Helm, *P.* [3] 11, 229). When amber is distilled, succinic acid and oil of amber are got. The latter (110°–260°) is a mixture of terpenes (Pelletier a. Walter, *A. Ch.* [3] 9, 89).

AMBREÏN. [25°–30°]. Extracted from ambergris by hot alcohol. Ambergris is found in the intestines of the spermaceti whale in tropical climates, and also floating in the sea. Ambreïn is insol. water, v. sol. alcohol or ether, neutral to litmus. It cannot be saponified. It greatly resembles cholesterin (Pelletier, *A.* 6, 24; *J. Ph.* 5, 49).

AMENYL GLYCERIN *v.* TRI-OXY-PENTANE.

AMENYL-VALERIC ACID *v.* DECENOIC ACID.

AMETHENIC ACID $C_7H_{14}O_2$ (185°–230°). By oxidation of diamylene with chromic mixture (Schneider, *A.* 157, 209).

Properties.—A light oil.

Salts.—SrA'_2, 8aq: needles.—ZnA'_2: warts; aqueous solution forms a gelatinous pp. on heating.—AgA': difficultly soluble pulverulent pp.

AMIC ACIDS. Bodies represented by the formula $X''(CO_2H).CO.NH_2$, being at once amide and acid, *e.g.* oxamic acid.

AMIDES. Bodies derived from ammonia by displacing one-third of its hydrogen by a monovalent acid radicle (Gerhardt a. Chiozza, *A. Ch.* [3] 46, 129). When two-thirds of the hydrogen is displaced by a divalent radicle the product is called an imide, but if the same amount of hydrogen is displaced by two monovalent radicles the product is still called an amide. If the whole of the hydrogen is displaced the product is also called an amide unless it is displaced by one trivalent radicle, when it is called a nitrile.

Amides derived from ammonia by displacing one-third of the hydrogen by an acid radicle, *e.g.* $NH_2.CO.X$, may also be looked upon as derived from mono-basic acids, X.CO.OH, by displacement of OH by NH_2.

Di-basic acids, $Y''(CO.OH)_2$, form, in a similar way, first amic acids, $Y''(CO.OH)(CO.NH_2)$, then di-amides, $Y''(CO.NH_2)_2$. Thus a di-amide may be considered to be derived from two molecules of ammonia by displacing one-third of the hydrogen by a di-valent acid radicle.

Formation.—1. By action of ammonia on ethers: $X.CO.OEt + NH_3 = X.CO.NH_2 + HOEt$.—2. By the action of ammonia on acid chlorides:

$$X.CO.Cl + 2NH_3 = X.CO.NH_2 + NH_4Cl.$$

3. By the dehydration of ammonium salts: $X.CO.ONH_4 - H_2O = X.CO.NH_2$. The rate at which this decomposition is brought about by heat has been studied by Menschutkin (*C. R.* 98, 1049).—4. By action of NH_3 on anhydrides:

$$(X.CO)_2O + 2NH_3 = X.CONH_2 + X.CO.ONH_4.$$

The anhydrides of di-basic acids are converted by this reaction into amic acids or imides.—5. From nitriles and cold conc. hydrochloric acid $XCN + H_2O = X.CO.NH_2$.—6. From nitriles, hydrogen peroxide, and very dilute KOH (Radziszewski, *B.* 18, 355).—7. Prepared by heating acids with ammonic sulphocyanide for three or four days, *e.g.*:

$$NH_4SNC + 2HOAc = 2AcNH_2 + COS + H_2O$$

(J. Schulze, *J. pr.* [2] 27, 512).

Properties.—The amides are usually solid, and their melting-points serve to identify the several acids. They are neutral to litmus, but form compounds with acids; their typical hydrogen can in many cases be displaced by metals (Ag or Hg). The typical hydrogen can be displaced by alkoyls, by treatment with acid chlorides, but heating with alkyl iodides does not result in the introduction of alkyls unless sodium has been previously introduced. Alkylated amides can be formed by the action of alkylamines upon acid chlorides or ethers.

Reactions.—1. Converted by dehydration (*e.g.* with P_2O_5) into nitriles: $X.CO.NH_2 = X.C{:}N + H_2O$.
2. Converted into acids by boiling *potash*, boiling dilute HCl, fuming HNO_3, or *nitrous acid*:

$$X.CO.NH_2 + HNO_3 = X.CO.OH + H_2O + N_2O$$

(Franchimont, *R.* 2, 343).

$$X.CO.NH_2 + HNO_2 = X.CO.OH + H_2O + N_2.$$

3. One of the typical atoms of hydrogen may be displaced by *halogens*; when *bromine* and *alkalis* are both present, compounds of the form X.CO.NKBr and $X.CO.NKBr_3$ are produced; these readily split up into KBr and cyanic ethers XNCO (Hofmann, *B.* 17, 1406; 18, 2734).
4. *Phosphorus pentachloride* reacts thus:

$$X.CO.NH_2 + PCl_5 = X.CCl_2.NH_2 + POCl_3.$$

The resulting compound splits off HCl giving $X.CCl_2NH_2 = HCl + XCCl{:}NH$ a chloro-imide and $X.CCl{:}NH = HCl + XC{:}N$.—5. PCl_5 acts upon alkylated amides, forming compounds with twice as many carbon atoms in the molecule. Thus $CH_3.CONHEt$ gives $CH_3CCl{:}NEt$ which then acts thus:

$$2CH_3CCl{:}NEt = NEt{:}CCl.CH_2.CMe{:}NEt + HCl.$$

$CH_3.CONHPh$ acts similarly, while PhCO.NHPh and $CCl_3CONHEt$ form only chloro-imides. Formanilide, HCONPhH does not produce NPh:CCl.CH:NPh but NPh:CH.NPhH, di-phenyl-formamidine (Wallach, *A.* 184, 1; 214, 193).

The HCl liberated in the decomposition

$$X.CCl_2.NHY = HCl + XCCl{:}NY$$

may often convert undecomposed amide into amidine $2X.CO.NHY + HCl =$

$$XCO_2H + XC(NY)(NHY)HCl.$$

Amidines may also be formed thus:

$$XCONHY + XCCl_2NHY = XC(NY)(NHY)HCl + XCOCl.$$

6. Heated with *alcohol* they form alkyl-ammonium salts:

$$X.CO.NH_2 + HOEt = X.CO.O.NH_3Et$$
$$X.CO.NHEt + HOEt = X.CO.O.NH_2Et_2$$
$$X.CO.NEt_2 + HOEt = X.CO.O.NHEt_3$$

(Baubigny, *C. R.* 95, 646).—7. $ZnEt_2$ acts thus:

$$X.CO.NH_2 + ZnEt_2 = X.CO.NZn + 2HEt$$
$$Y''.(CO.NH_2)_2 + ZnEt_2 = Y''.C_2O_2N_2H_2Zn + 2HEt.$$

These compounds are decomposed by water, with reproduction of the amide (H. Gal, *C. R.* 96, 1315).—8. *Phenyl-hydrazine* reacts thus: $PhNH.NH_2 + NH_2.CO.X = PhNH.NH.CO.X + NH_3$ (F. Just, *B.* 19, 1201).—9. Dry HCl converts primary into secondary amides:

$$2NAcH_2 + HCl = NAc_2H + NH_4Cl$$

AMIDINES. The name is applied to compounds that contain amidogen and imidogen attached to the same atom of carbon. Thus, $CH_3.C(NH).NH_2$ is called acetamidine, that is to say, an imide derived from acetamide, while $C_6H_5C(NH)NH_2$ is called benz-amidine, the imide of benzamide. Other names for these

bodies are ethenyl amidine, benzenyl amidine, ethenyl imid-amide, benzenyl imid-amide, acet-imid-amide, benz-imid-amide. The advantage of the imido-amide nomenclature is chiefly seen in naming derivatives, thus $CH_3.C(NEt).NH_2$ and $CH_3.C(NH).NEtH$ may be called acet-ethyl-imido-amide, and acet-imido-ethyl-amide, respectively. But the advantage so gained is lost in the great lengthening of the names, and both bodies will therefore be called ethyl-acetamidine in this dictionary. They might be distinguished as tertiary and secondary ethyl-acetamidine respectively.

Dibasic acids can give rise to a variety of amide-imides, for which Wallach (*A.* 214, 256) proposes the following nomenclature:—

$R<^{CO.NH_2}_{C(NH).NH_2}$ amid-amidine.

$R<^{C(NH).NH_2}_{C(NH).NH_2}$ amidine.

$R<^{CO}_{C(NH)}>NH$ imid-imidine.

$R<^{C(NH)}_{C(NH)}>NH$ imidine.

Formation.—1. Amidines are formed by the action of amines on thio-amides or nitriles: $Ph.CN + NPh_2H = Ph.C(NH).NPh_2$ (Bernthsen, *A.* 184, 290, 321).—2. By the action of amines on the compounds ($X.CCl:NH$ or $X.CCl:NY$) formed by the action of PCl_5 on amides (Wallach, *B.* 8, 1575).

Reactions.—1. H_2S forms thio-amides:
$Ph.C(NPh).NPhH + H_2S = Ph.CS.NPhH + H_2NPh$
$Ph.C(NH).NPhH + H_2S = Ph.CS.NPhH + NH_3$.
Another reaction also takes place:
$Ph.C(NH).NPhH + H_2S = Ph.CS.NH_2 + NPhH_2$.
This may be explained by supposing an intermediate compound, $Ph.C.(SH)(NH_2).NPhH$, to be formed by addition of H_2S.

2. CS_2 acts thus:
$Ph.C(NH).NPhH + CS_2 = Ph.CS.NPhH + HNCS$
$Ph.C(NH).NPh_2 + CS_2 = Ph.CS.NPh_2 + HNCS$
$Ph.C(NPh).NPhH + CS_2 = Ph.CS.NPhH + PhNCS$

3. Action of *aceto-acetic ether*, *v.* p. 19.

The reactions of the amidines are further described in such articles as FORMAMIDINE, ACETAMIDINE, BENZAMIDINE, MANDEL-AMIDINE, PHENYL-ACETAMIDINE, and PHENYL-BENZAMIDINE.

AMIDO-ACETANILIDE *v.* Acetyl-PHENYLENE-DI-AMINE.

AMIDO-ACETIC ACID *v.* GLYCOCOLL.

Acetyl derivative v. ACETURIC ACID.

Benzoyl derivative v. HIPPURIC ACID.

AMIDO-ACETO-ACETIC ACID *v.* ACETO-ACETIC ACID.

AMIDO-ACETO-NAPHTHALIDE *v.* ACETYL-NAPHTHYLENE DI-AMINE.

AMIDO-ACETOPHENONES C_8H_9NO *i.e.* $C_6H_4(NH_2).CO.CH_3$ *Amidophenyl methyl ketone.*

o-Amido-acetophenone (c. 249°).

Formation.—1. By reduction of *o*-nitro-acetophenone (Gevekoht, *B.* 15, 2086; *A.* 221, 326).—2. By action of conc. H_2SO_4 on a solution of *o*-amido-phenyl-acetylene (Baeyer a. Bloem, *B.* 15, 2154).—3. By boiling *o*-amido-phenyl-propiolic acid with water (B. a. B.).

Preparation.—*o*-Amido - phenyl - acetylene (50 g.) is slowly dropped into conc. H_2SO_4 (600 c.c.) diluted with water (200 c.c.). After half an hour, the mixture is poured upon ice; neutralised with Na_2CO_3; distilled with steam; and the distillate extracted with ether. 50 p.c. of the theoretical yield is got (Baeyer a. Bloem, *B.* 17, 964). *Properties*.—Thick volatile oil.

Oxim [148°] (Münchmeyer, *B.* 20, 512).

Salts. — $B'H_2SO_4$: needles. — $B'HClSnCl_2$: needles, sol. alcohol.— $B'_2H_2PtCl_6$: yellow pp.

Reaction.—By boiling with alcoholic *aceto-phenone* and some NaOHAq it is converted into flavolin or phenyl-methyl-quinoline (O. Fischer, *B.* 19, 1036): $C_6H_4(NH_2).CO.Me + Ph.CO.CH_3 =$

$$H_2O + C_6H_4<^{CMe:CH}_{N\ :\ CPh}$$

Acetyl derivative $C_6H_4(NHAc).CO.CH_3$. [77°]. Silky needles (from benzoline). Sol. alcohol, ether, and hot water, sl. sol. cold water.

m-Amido-acetophenone [93°]. Formed by reducing the nitro compound by Sn and HCl (Buchka, *B.* 10, 1714; Hunnius, *B.* 10, 2009; Engler, *B.* 11, 932). Short yellow pyramids, sol. alcohol, and ether.

Salt.—B'HCl: long pointed crystals.

p-Amido-acetophenone [106°].

Formation.—From the nitro compound (*q.v.*) by Sn and HCl (Drewson, *A.* 212, 162).

Preparation.—Aniline (2 pts.), $ZnCl_2$ (3 pts.), and Ac_2O (5 pts.) are boiled together for 5 hours; the resulting acetyl derivative is saponified. Yield 55 p.c. of the theoretical (Klingel, *B.* 18, 2687).

Properties.—Long fan-like crystals (from water). V. sol. alcohol, ether and hot water, sl. sol. cold water, benzene, and benzoline.

Salts.—B'HCl: needles.—$B'_2H_2PtCl_6$: slender yellow needles.—$B'_2H_2SO_4$: needles.—$B'_2H_2C_2O_4$: crystals, v. sol. alcohol.

Acetyl derivative $C_6H_4(NHAc).CO.CH_3$. [167°]. Small needles, v. sol. alcohol, and hot water, sl. sol. cold water.

Ethyl derivative v. ETHYL-AMIDO-ACETO-PHENONE.

Benzyl derivative v. BENZYL - AMIDO-ACETOPHENONE.

AMIDO ACIDS.—Amidogen, when attached to carbon in an acid, behaves as it does in amides (*q.v.*) or as in amines (*q.v.*) according as that carbon does or does not belong to carbonyl; in the former case the compound is classed as an amic acid (*q.v.*), the term 'amido acid' is usually restricted to the latter class of bodies.

Formation.—1. From the halogen derivatives of fatty acids, or their ethers, by the action of ammonia.—2. From the nitro-derivatives of (aromatic) acids by reduction.—3. From aldehydes, by action of hydric cyanide and NH_3:
$X.CHO + HCN + NH_3 = X.CH(NH_2)CN + H_2O$.
The nitrile is then converted into amide by conc. HCl, and this is saponified by hot dilute HCl. In this way α-amido acids may be prepared; alkylamido acids can be formed by using alkylamines instead of ammonia (Tiemann, *B.* 14, 1982; Stephan, *C. C.* 1886, 470).

Properties.—Neutral bodies which combine both with acids and bases. Their neutrality is probably due to self-saturation, as may be represented by a doubled formula:

$$\begin{array}{c} R.CH.NH_3.O.CO \\ | \qquad\quad | \\ CO.O.NH_3.CH.R. \end{array}$$

Reactions.—1. Converted by *nitrous acid*

into oxy-acids (*v.* p. 57, l. 6); di-azo derivatives (*q. v.*) are first formed, and this formation may be utilised as a test for amido-acids (Curtius, *B.* 17, 959).—2. When heated with *lime* or *baryta*, they split off CO_2 forming amines. This separation of CO_2 sometimes occurs in *formation* 2: thus $C_6H_3(NO_2)Br(CO_2H)$ [4:2:1] reduces to *m*-bromo-aniline (Scheufelen, *A.* 231, 176); $C_6H_3(NO_2)_2CO_2H$ [4:1:2] reduces to *m*-phenylene diamine (Wurster, *B.* 7, 149; Griess, *B.* 7, 1225); while $C_6H_3(NO_2)(CO_2H)_2$ [4:1:2] becomes *m*-amido-benzoic acid. In all these cases the CO_2 is split off from the position *para* to NO_2.—3. AcCl forms acetyl-amido acids. 4. Excess of *methyl iodide*, in presence of KOH, converts (fatty) amido acids into ammonium iodides:

$$CH_2(NH_2).CO_2H + 3MeI + 3KOH = CH_2(NMe_3I).CO_2K + 2KI + 3H_2O$$

(Körner a. Menozzi, *G.* 13, 350). *p*-Amido-benzoic acid is converted by MeI and KOH into the betaïne $C_6H_4<{NMe_3 \atop CO.O}>$, while EtI only forms di-ethyl-amido-benzoic acid (Michael a. Wing, *Am.* 7, 195).—5. Saturated with cupric hydroxide, suspended in hot water, they form blue solutions from which on cooling the copper salt separates. This occurs with leucine, glutamic acid, and aspartic acid. In the case of leucine, a portion remains dissolved, forming a blue mother liquor. In the case of mixtures of amido-acids, the copper salts are not so readily ppd., for they seem to render one another soluble (Schulze a. Barbieri, *J. pr.* [2] 27, 351).—6. The methods of displacing amidogen by halogens in aromatic bodies are mentioned under AMINES.

AMIDO-ACRYLIC ACID $C_3H_5NO_2$ *i.e.* $CH(NH_2):CH.CO_2H$, is formed by the action of alcoholic ammonia on *β*-chloracrylic acid at 100° (Pinner a. Bischoff, *A.* 179, 97). H. W.

AMIDO-ALCOHOLS or Alkamines (*q. v.*) are formed by action of bases on chlorhydrins or on alkylene oxides, *e.g.*:

$$CH_2Cl.CH_2OH + NH_3 = CH_2(NH_2HCl).CH_2.OH,$$

and

$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}>O + NMe_3 + H_2O = CH_2(NMe_3OH).CH_2OH.$$

V. OXY-ETHYL-AMINE, NEURINE, &c.

AMIDO-ALIZARIN *v.* OXY-AMIDO-ANTHRAQUINONES.

DI-AMIDO-AMARINE *v.* *Amarine* under BENZOIC ALDEHYDE.

AMIDO-AMYL ALCOHOL *v.* OXY-AMYL-AMINE.

AMIDO-AMYL-BENZENE $C_{11}H_{17}N$ *i.e.* $C_6H_4(C_5H_{11})NH_2$. (258°) (C.); (260°-265°) (H.). An oil. Formed by heating amyl-aniline hydrochloride at 320° (Hofmann, *B.* 7, 529), or by heating aniline with amyl alcohol and $ZnCl_2$ at 270° (Calm, *B.* 15, 1643).

Salts.—$B'_2H_2SO_4$: silky needles.—$B'_2H_2PtCl_6$: slender orange-yellow needles.

Benzoyl derivative $C_6H_4(C_5H_{11})NHBz$. [c. 149°]. Pearly plates; sol. alcohol, ether, benzene.

AMIDO-ANISIC ACID *v.* *Methyl*-OXY-AMIDO-BENZOIC ACID.

AMIDO-ANISOL *v.* *Methyl*-AMIDO-PHENOL.

AMIDO-ANTHRACENE *v.* ANTHRAMINE.

AMIDO-ANTHRAQUINONES $C_{14}H_9NO_2$. M.w. 223. Three have been described, but theory indicates only two; (*a*) and *m*- are perhaps identical.

***o*-Amido-anthraquinone**

$$C_6H_4<{CO(1) \atop CO(6)}>C_6H_3.NH_2\ (2).\quad [241°].$$

Formation.—1. By reducing *o*-nitro-anthraquinone (Roemer, *B.* 15, 1790).

Properties.—Ruby-red iridescent needles; may be sublimed. Sol. alcohol, ether, benzene and HOAc, forming orange liquids, v. sl. sol. water. It is a weak base, dissolving in conc. HCl. Converted by nitrous acid into *erythro*-oxy-anthraquinone.

Salt.—B'HCl: unstable white needles.

Acetyl derivative $C_{14}H_7O_2NAcH$ [202°]. Orange-red needles, sol. alcohol and cold HClAq.

(*a*)-Amido-anthraquinone [254°].

Formation.—1. From bromo-nitro-anthraquinone (Claus a. Hertel, *B.* 14, 980) or from di-bromo-nitro-anthraquinone (Claus a. Dierenfellner, *B.* 14, 1334) by sodium-amalgam.—2. From (*a*)-nitro-anthraquinone and sodium-amalgam (Böttger a. Petersen, *A.* 166, 149).

Properties.—Red needles, may be sublimed. Sol. benzene and chloroform, sl. sol. alcohol, and ether. Differs from the preceding by insolubility even in fuming HClAq.

***m*-Amido-anthraquinone**

$$C_6H_4<{CO\ (1) \atop CO\ (6)}>C_6H_3NH_2\ (3).\quad [302°].$$

Formation.—1. From anthraquinone *m*-sulphonic acid and NH_3Aq at 200° (Perger, *B.* 12, 1566; according to Bouchardat, *Bl.* 33, 264, this reaction produces amido-oxy-anthraquinone) 2. From its acetyl derivative, which is got by oxidising acetyl-anthramine by CrO_3 in glacial HOAc (Liebermann, *A.* 212, 61).

Properties.—Red needles. Sol. aqueous HCl, insoluble in alkalis. By the action of HNO_2 and boiling alcohol it is converted into anthraquinone.

Acetyl derivative $C_{14}H_7O_2NAcH$. [257°] (P.); [263°] (L.); colourless needles.

Di-amido-anthraquinones $C_{14}H_{10}N_2O_2$ *i.e.* $C_{14}H_6O_2(NH_2)_2$.

(*a*)-Di-amido-anthraquinone [236°].

Formation.—1. From (*a*)-di-nitro-anthraquinone either (*a*) by ammonic sulphide, (*b*) by aqueous NH_3 at 200°, nitrogen coming off (J. Fischer, *J. pr.* [2] 19, 209), or (*c*) by $SnCl_2$ and NaOHAq (Böttger a. Petersen, *A.* 160, 148). 2. By reduction of tetra-bromo-di-nitro-anthraquinone (Claus a. Hertel, *B.* 14, 981).

Properties.—Red needles (from ether), with greenish reflex (when sublimed). V. sl. sol water, m. sol. alcohol, ether or acetone, v. sol. benzene. The solutions are purple. Hardly soluble in dilute acids; does not form salts.

Reactions.—1. *Nitrous acid* passed into its alcoholic solution forms anthraquinone (B.a.P.). 2. *Nitrous acid* passed into its ethereal solution forms a brownish-violet powder, $C_{14}H_8N_4O_4$, which detonates at about 68° (B.a.P.).—3. *Potash-fusion* produces alizarin (Böttger a. Petersen, *B.* 4, 778), or some similar body (Liebermann, *B.* 4, 231, 779).

(*β*)-Di-amido-anthraquinone [above 300°].

Formation.—1. By boiling (*β*)-di-nitro-anthraquinone with $SnCl_2$ and NaOHAq (Schmidt, *J. pr.* [2] 9, 266).

Properties.—Reddish-brown powder; sub-

limes in dark red needles. Sl. sol. water, v. sol. alcohol, ether, and benzene, forming red solutions. Sol. conc. acids, but re-ppd. unaltered by water.

(γ)-**Di-amido-anthraquinone.**

Preparation.—Alizarin (20 grms.) is heated for 7 hours at 170° with ammonia solution (200 c.c., S.G. ·915). Alcohol extracts the greater portion (6·2 grms.) of the insoluble residue (7·3 grms.). Water is added to the alcohol, and the pp. is dried *in vacuo* and washed with ether (H. v. Perger, *J. pr.* [2] 18, 135).

Properties.—Indigo-blue powder, which acquires a coppery lustre when rubbed. When HCl is added to its blue alcoholic solution (at 0°), the liquid turns cherry-red and deposits brown-red needles of a hydrochloride, which, however, is so unstable as to be reconverted into the amorphous blue base by merely washing with water. It does not dye mordanted goods.

Reactions.—1. Boiled with *potash* it is converted into oxy-amido-anthraquinone (*q. v.*): $C_{14}H_6O_2(NH_2)_2 + KOH = C_{14}H_6O_2(OK)NH_2 + NH_3$. 2. Similar reaction by boiling HCl.—3. *Fused with potash*, or heated with HCl at 250°, forms alizarin.—4. By passing N_2O_3 into its alcoholic solution until the blue colour is changed to pure yellow, it is converted into erythro-oxy-anthraquinone, which is thrown down when water is added. Yield 95 p.c.

(δ)-**Di-amido-anthraquinone**

$$(3)\ NH_2.C_6H_3{<}{CO\ (1) \atop CO\ (2)}{>}C_6H_3.NH_2\ (6).$$

[above 300°].

Formation.—By reducing the corresponding di-nitro-anthraquinone, [above 300°] (Roemer, *H.* 16, 366).

Properties.—Splendid red metallic needles (by sublimation). Sl. sol. alcohol, ether, acetone, and chloroform, with orange colour; v. sl. sol. water. Very weak base.

Reactions.—1. Boiling *potash* has no action. 2. *Diazotisation* followed by boiling with water converts it into anthrarufin (*v.* Di-oxy-anthraquinone).

Di-acetyl derivative $C_{14}H_6O_2(NHAc)_2$. Reddish yellow needles, v. sol. alcohol, and ether.

AMIDO-ANTHRAQUINONE SULPHONIC ACIDS

$C_{14}H_9NSO_5$ *i.e.* $C_{14}H_6O_2(NH_2).SO_3H$

o-**Amido-anthraquinone sulphonic acid**

$$C_6H_4{<}{CO(1) \atop CO(2)}{>}C_6H_2(NH_2)(SO_3H)\ [1:6:2:4].$$

Formed by reducing nitro-anthraquinone sulphonic acid (Lifschutz, *B.* 17, 899). Silvery needles.

(α)-**Amido-anthraquinone sulphonic acid.**—Prepared by reducing (α)-nitro-anthraquinone sulphonic acid (Claus, *B.* 15, 1519). Sol. dilute acids, and in hot water, sl. sol. cold water, alcohol, and ether.

Salts.—$NaA'\,1\frac{1}{2}aq$: small red needles.—$CaA'_2\,5aq$: red needles.—$BaA'_2\,3\frac{1}{2}aq$: slender red needles.—$CuA'_2\,7aq$: yellowish-red needles.

(β)-**amido-anthraquinone sulphonic acid.**—Formed by reducing the lead salt of (β)-nitro-anthraquinone sulphonic acid with H_2S (Claus, *B.* 15, 1520). Red powder; v. sol. water forming a red solution, sl. sol. alcohol, insol. ether. A weak acid.

(α)-**Di-amido-anthraquinone sulphonic acid**

$C_{14}H_{10}N_2SO_5$ *i.e.* $C_{14}H_5O_2(NH_2)_2SO_3H$. Obtained from (α)-di-amido-anthraquinone by means of H_2SO_4 containing dissolved SO_3 (30 p.c.); ppd. by water. The solution is a splendid red. It may be crystallised from alcohol. Sol. glacial HOAc, and in acetic ether. Insol. ether, benzene or benzoline. On passing nitrous gas into its alcoholic solution anthraquinone (α)-sulphonic acid is formed. *Potash-fusion* forms alizarin.

Salt.—BaA'_2: insol. cold water (v. Perger, *J. pr.* [2] 19, 209).

AMIDO-ARACHIC ACID

$C_{20}H_{41}NO_2$ *i.e.* $C_{20}H_{39}(NH_2)O_2$. [59°].

From nitro-arachic acid and $SnCl_2$ (Tassinari, *B.* 11, 2031). Sl. sol. ether, m. sol. alcohol. Combines with neither acids nor bases.

AMIDO-AZO-COMPOUNDS *v.* Azo compounds.

AMIDO-BENZALDEHYDE *v.* Amido-benzoic aldehyde.

AMIDO-BENZAMIDE *v.* Amido-benzoic acid.

AMIDO-BENZ-ANILIDE *v.* Amido-benzoic acid.

AMIDO-BENZENE *v.* Aniline.

Di-amido-benzene *v.* Phenylene di-amine.

con-**Tri-amido-benzene** $C_6H_9N_3$ *i.e.* $C_6H_3(NH_2)_3$ [1:2:3]. [103°]. (336° cor.). Obtained by distilling tri-amido-benzoic acid with pounded glass (Salkowsky, *A.* 163, 23). Crystalline; v. sol. water, alcohol, and ether. Its aqueous solution is alkaline and gives with Fe_2Cl_6 first a violet, then a brown pp.; hypochlorites and nitrites give brown pps. Reduces cold ammoniacal $AgNO_3Aq$. H_2SO_4 containing a little HNO_3 forms a blue colour.

Salts.—$B'''2HCl$: sl. sol. conc. hydric chloride B''.—$H_2SO_4\,2aq$.

i-**Tri-amido-benzene** $C_6H_3(NH_2)_3$. [1:2:4]. [below 100°]. (c. 340°).

Formation.—1. From (α)-di-nitro-aniline, Sn, and HCl (Salkowsky, *A.* 174, 265).—2. From di-amido-azo-benzene *p*-sulphonic acid by Sn and HCl (Griess, *B.* 15, 2196).—3. From chrysoïdin by reduction (Witt, *B.* 10, 658).—4. From di-nitro-benzene-azo-benzene sulphonic acid by reduction (Janovsky, *M.* 5, 159).

Properties.—Colourless plates. V. sol. water, and alcohol, sl. sol. ether. Gives a red (G.) or green (J.) colour with Fe_2Cl_6Aq.

Salts.—$B''H_2SO_4$. Needles or prisms; sl. sol. cold water, v. sl. sol. alcohol.—$B''2HCl$ [133°]: needles (Hinsberg, *B.* 19, 1253).

s-**Tri-amido-benzene** $C_6H_3(NH_2)_3$ [1:3:5] (?) The tin double salt, $C_6H_3(NH_2)_3(HCl)_3SnCl_2$, of this base may be got from tri-nitro-benzene (got by nitration of di-nitro-benzene) by Sn and HCl (Hepp, *A.* 215, 348). But after removing the tin by H_2S, the hydrochloride of the base resinifies, NH_4Cl being formed, although by evaporation in vacuo over H_2SO_4 a very soluble white hydrochloride may be got. It gives no colour with Fe_2Cl_6.

Tetra-amido-benzene $C_6H_2(NH_2)_4$ [1:2:4:5] Formed by reduction of di-nitro-*m*-phenylene diamine with tin and $SnCl_4$. The base is extremely oxidisable. An aqueous solution of the hydrochloride when treated with Fe_2Cl_6 gives a pp of brown needles of $C_6H_2(NH_2)_2(NH)_2H_2Cl_2$.

Salts.—$B^{iv}H_4Cl_4$: v. sol. water, sl. sol. conc aqueous HCl.—$B^{iv}_2(H_2SO_4)_3$: sparingly solubl

large plates.—$B^{iv}H_2SO_4$: long sparingly soluble needles (Nietzki a. Hagenbach, *B.* 20, 334).

AMIDO-BENZENE SULPHONIC ACIDS $C_6H_7NSO_3$ *i.e.* $C_6H_4(NH_2).SO_3H$. *Aniline sulphonic acids.* In the bromination of these acids Br never takes a position ... to NH_2 (Limpricht, *A.* 191, 252).

***o*-Amido-benzene sulphonic acid** $C_6H_4(NH_2)SO_3H$ [1:2]. S. 1 at 7°.

Formation.—1. From *o*-nitro-benzene sulphonic acid (Berndsen a. Limpricht, *A.* 177, 98).—2. From *m*-bromo-benzene sulphonic acid by nitration and reduction (Thomas, *A.* 186, 128).

Properties.—Dull white crystals like rhombohedra. Also, as HA′½aq, in transparent shining prisms with many faces. Bromine added to a very dilute solution of the barium salt produces H_2SO_4, tri-bromo-aniline and (1, 4, 5)- bromo-amido-benzene sulphonic acid.

Salts (Bahlmann, *A.* 186, 308).—KA′½aq: prisms.—AgA′: needles.—BaA'_2 (L. a. B.).—BaA'_2 2aq (T.).—PbA'_2 ½aq. S. 3·4 at 6°.

***m*-Amido-benzene sulphonic acid** $C_6H_4(NH_2)SO_3H$ [1:3]. S. 1·2 at 7°; 1·5 at 15°. From *m*-nitro-benzene sulphonic acid by reduction (Laurent, *C. R.* 31, 538; Schmitt, *A.* 120, 164; Berndsen, *A.* 177, 82). Also from (1, 2, 4)- bromo-amido-benzene sulphonic acid and HIAq at 120° (Goslich, *A.* 180, 102).

Long slender radiating needles. Also, with 1½aq in monoclinic prisms. Sl. sol. cold water, v. sol. hot water, insol. alcohol, and ether. Aqueous solution turns red in air. When heated it decomposes without fusion.

Reactions.—1. *Bromine* added to an aqueous solution produces no tri-bromo-aniline, but (1, 3, 4, 6)- di-bromo-amido-benzene sulphonic acid, (1, 3, 5, 4, 6)- tri-bromo-amido-benzene sulphonic acid, and bromanil. *Chlorine* acts similarly (Beckurts, *A.* 181, 211).—2. Does not produce quinone when *oxidised* (Meyer a. Stüber, *A.* 165, 168).

Salts: BaA'_2 6aq.—PbA'_2.

Amide $C_6H_4(NH_2).SO_2NH_2$. [142°]. From *m*-nitro-benzene sulphamide, conc. NH_3Aq, and H_2S (Limpricht a. Hybbeneth, *A.* 221, 204). White plates or long needles (from water).

Hydro-chloride.—$C_6H_4(NH_2Cl)SO_2NH_2$. [235°]. Needles.

Nitrous acid, passed into a cold mixture of the amide with a little HNO_3, produces a di-azo nitrate, $C_6H_4(N_2NO_3).SO_2NH_2$, benzene sulphamide, and a diazo-amido compound $C_6H_4(SO_2NH_2).N_2.NH.C_6H_4.SO_2NH_2$; the latter, [183°], is insol. water, and is split up by HClAq into $C_6H_4(SO_2NH_2)Cl$, N_2, and $NH_2.C_6H_4.SO_2NH_2$.

***p*-Amido-benzene sulphonic acid** $C_6H_4(NH_2)SO_3H$ [1:4]. *Sulphanilic acid.* S. ·6 at 6°.

Formation.—1. By heating oxanilide or aniline with H_2SO_4 (Gerhardt, *J. Ph.* [3] 10, 5).—2. By heating aniline with fuming H_2SO_4 at 190° (Buckton a. Hofmann, *C. J.* 9, 259; R. Schmitt, *A.* 120, 129).—3. From aniline and *p*-phenol sulphonic acid (Pratesi, *B.* 4, 970; Kopp, *B.* 4, 978).—4. By reducing *p*-nitrobenzene sulphonic acid.—5. By heating aniline ethyl-sulphate (Limpricht, *A.* 177, 80).

Preparation.—Aniline (93 g.) is slowly poured into H_2SO_4 (50 g.) diluted with water. The solution is evaporated and the dried sulphate is mixed with H_2SO_4 (50 g.) and sand, and heated in a dish, with constant stirring, until it becomes solid. Crystallised from water.

Properties.—Plates or trimetric prisms (with aq); monoclinic (with 2 aq).

Reactions.—1. *Bromine-water* gives tri-bromo-aniline and (1,3,2,5)-di-bromo-amido-benzene sulphonic acid.—2. *Oxidised* to quinone by $K_2Cr_2O_7$ and H_2SO_4Aq (Meyer a. Ador, *A.* 159, 7) or by MnO_2 and H_2SO_4 (Schrader, *B.* 8, 759).—3. $KMnO_4$ converts its potassium salt into the azo derivative $C_6H_4(SO_3K).N_2.C_6H_4.SO_3K$ (Laar, *J. pr.* [2] 20, 264), the corresponding azoxy-compound being also formed (Limpricht, *B.* 18, 1420).—4. PCl_5 forms $C_6H_4(SO_2Cl).NH.POCl_2$ [158°], which is converted by alcohol into $C_6H_4(SO_3Et).NH.PO(OEt)_2$ [102°], and by methyl alcohol into $C_6H_4(SO_3Me).NH.PO(OMe)_2$ [114°]. The former is split up by boiling into alcohol, sulphanilic acid, and hydro-di-ethylic phosphate. *V.* also DI-BROMO-AMIDO-BENZENE SULPHONIC ACID.

Salts.—NaA′ 2aq. — KA′ 1½aq: triclinic prisms.—NH_4A' 1½aq.—BaA'_2 3½aq.—CuA'_2 4aq. —*Aniline sulphanilate* C_6H_7N2HA'. Gives off all its aniline at 100°.

Acetyl derivative $C_6H_4(NHAc)(SO_3H)$—obtained as the sodium salt by boiling sodium sulphanilate with acetic anhydride. The free acid has not been isolated, as it readily splits off acetic acid on evaporation of its solution. The sodium salt (A′Na) forms small colourless prisms very soluble in water, but less in alcohol (Nietzki a. Benckiser, *B.* 17, 707).

Amido-benzene di-sulphonic acids.

I. $C_6H_7NS_2O_6$, *i.e.* $C_6H_3(NH_2)(SO_3H)_2$. [1:3:4?] From *m*-amido-benzene sulphonic acid and fuming H_2SO_4 at 180° (Drebes, *B.* 9, 552; Zander, *A.* 198, 21).—Rhombic octahedra, v. e. sol. water or alcohol.

Salts.—$(NH_4)_2A''$ aq.—K_2A'' aq.—KHA″.—BaA″ 1½aq.—$BaH_2A''_2$; S. 2·9 at 8°.—PbA″ aq.—$PbH_2A''_2$.

II. $C_6H_3(NH_2)(SO_3H)_2$ 2aq. [1:3:5]. From the corresponding nitro acid by reduction (Heinzelmann, *A.* 188, 167). Four or six sided columns, v. sol. water, and alcohol, insol. ether. *Bromine water* gives a pp. of bromanil.

Salts. — $(NH_4)_2A''$aq. — HNH_4A''xaq. — K_2A'' 3aq.—K_2A'' 4aq.—KHA″ aq.—BaA″ 3½aq. —$BaH_2A''_2$ 5aq.—PbA″ 3½aq.—$PbH_2A''_2$ 6aq. — Ag_2A''.

III. $C_6H_3(NH_2)(SO_3H)_2$ [1:2:4]. *Di-sulphanilic acid.*

Formation.—1. By heating sulphanilic acid with fuming H_2SO_4 at 170° for 6 hours (Buckton a. Hofmann, *A.* 100, 164).—2. By heating *o*-amido-benzene sulphonic acid with fuming H_2SO_4 at 180° (Zander, *A.* 198, 17).—3. By reducing the corresponding nitro acid (Heinzelmann, *A.* 188, 170).

Properties.—Minute (red) clumps (from water). V. sol. alcohol, insol. ether. *Bromine water* gives tri-bromo-aniline, bromo-amido-benzene di-sulphonic acid, and di-bromo-amido-benzene sulphonic acid.

Salts.—The acid salts are less soluble in water than the neutral ones.—$(NH_4)_2A''$ aq: small

hexagonal prisms.—$NH_4HA''2aq$: clumps.—$K_2A''aq$.—$KHA''aq$: silky needles.—$BaA''3aq$: four-sided plates. — $BaH_2A''_2aq$. — $CaA''2aq$: minute white needles. — $CaH_2A''_2$: slender needles.—$PbA''2aq$.—$PbH_2A''_2aq$: small prisms. — $PbH_2A''_26aq$. — Ag_2A'': prisms. — $AgHA''$: needles or plates.

Di-amido-benzene sulphonic acids $C_6H_8N_2SO_3$. *Phenylene-di-amine sulphonic acids.*

I. $C_6H_3(NH_2)_2(SO_3H)$ [1:2 or 5:3]. S. 1 at 10°. From the corresponding nitro acid (Sachse, *A.* 188, 148).—Rhombic tablets. V. sl. sol. alcohol, insol. ether. Turns brown in air. Metallic salts crystallise with difficulty.

Salts.—$HA'HCl$: needles.—$HA'HClSnCl_2$.—$HA'HBr$.—$H_2A'_2H_2SO_4aq$.—$HA'H_2SO_4\frac{1}{2}aq$.

II. $C_6H_3(NH_2)_2HSO_3$ [1:2:4].

Small colourless needles.

Preparation.—1 By sulphonation of *o*-phenylene-diamine.—2. By reduction of (1:2:4) nitro-amido-benzene sulphonic acid.

Salts.—$A'_2Ba + 5\frac{1}{2}H_2O$: easily soluble thin tables or needles.—$A'_2Ca + 3H_2O$: soluble tables or needles (Post and Hardtung, *B.* 13, 39; *A.* 205, 98).

III. $C_6H_3(NH_2)_2HSO_3$ [1:3:4].

Preparation.—1. By sulphonation of *m*-phenylene-diamine.—2. By reduction of nitro-amido-benzene sulphonic acid [1:3:4].

Dimorphous: monoclinic tables, $a:b:c = 1{\cdot}31:1:1{\cdot}36$, or triclinic prisms, $a:b:c = {\cdot}424:1:{\cdot}928$.

Salts.—$A'_2Ba\,6aq$: long soluble prisms. $A'_2Ca\,5aq$: soluble prisms or tables (Post a. Hardtung, *B.* 13, 40; *A.* 205, 104).

Di-amido-benzene di-sulphonic acid $C_6H_8N_2S_2O_6aq$ *i.e.* $C_6H_2(NH_2)_2(SO_3H)_2aq$. From the nitro acid by reduction (Limpricht, *B.* 8, 290). V. sol. water.

Salt.—$SnA''aq$: needles.

AMIDO-BENZENE PHOSPHONIC ACID $C_6H_8NPO_3$ *i.e.* $C_6H_4(NH_2)PO(OH)_2$. From the nitro acid, tin, and HCl. Slender needles (from water); v. sl. sol. water, v. sol. HClAq; insol. alcohol and ether. Salts.—$Na_2A''3aq$.—PbA''. CuA''.—Ag_2A'' (Michaelis a. Benzinger, *A.* 188, 282).

DI-AMIDO-BENZHYDROL *v.* DI-AMIDO-DI-PHENYL-CARBINOL.

AMIDO-BENZOIC ACIDS $C_7H_7NO_2$ *i.e.* $C_6H_4(NH_2).CO_2H$. M. w. 137. The following derivatives are described in special articles: NITRO-AMIDO-BENZOIC ACID, CHLORO-AMIDO-BENZOIC ACID, CHLORO-METHYL-AMIDO-BENZOIC ACID, METHYL-AMIDO-BENZOIC ACID, ETHYL-AMIDO-BENZOIC ACID, PHENYL-AMIDO-BENZOIC ACID.

***o*-Amido-benzoic acid** $C_6H_4(NH_2).CO_2H$ [1:2]. *Anthranilic acid.* [144°–145°].

Formation.—1. By reducing *o*-nitro-benzoic acid (Beilstein a. Kuhlberg, *A.* 163, 138).—2. By boiling indigo with KOHAq (Fritzsche, *A.* 39, 83).—3. From (1, 2, 3), or (1, 4, 5)-bromo-amido-benzoic acid by sodium-amalgam (Hübner a. Petermann, *A.* 149, 133).—4. From its acetyl derivative and boiling conc. HCl.—5. From isatoic acid (*q.v.*) and boiling conc. HCl.

Properties.—Plates, or rhombic crystals (Haushofer, *A.* 193, 233). May be sublimed. V. sol. water, and alcohol. Converted by *nitrous acid* into salicylic acid; and by *sodium-amalgam* into NH_3 and benzoic acid. HCl and $KClO_3$ form chloranil (Hofmann, *A.* 52, 65). Its *anhydride* is described as ANTHRANIL.

Salts.—$HA'HCl$: [91°]; needles (Kubel, *A.* 102, 236).—$HA'HNO_3$.—$(HA')_2H_2SO_42aq$: needles [188°].—$(HA')_2H_2SO_4aq$.—$(HA')_2H_2C_2O_4$.—BaA'_2: v. e. sol. water; sl. sol. alcohol.—PbA'_2.—CuA'_2.—AgA'.

Ethyl ether EtA'. (260°). Liquid; its hydrochloride, $EtA'HCl$, [170°], forms needles, insol. ether, and may be sublimed.

Reactions.—1. *Nitrous acid* produces salicylic acid (Gerland, *A.* 86, 143) or diazobenzoic acid (*v.* DI-AZO compounds).—2. KCNO converts the hydrochloride of *o*-amido-benzoic acid into uramido-benzoic acid (*q. v.*); *Potassium sulphocyanide* forms, similarly, thio-uramido-benzoic acid (*q. v.*).—3. *Phenyl cyanate* (*q. v.*) forms $NH_2.C_6H_4.CO.NPh.CO.NPhH$. — 4. *Cyanogen* passed into an aqueous solution forms $C_9H_7N_3O$ (Griess, *B.* 11, 1986), while in an alcoholic solution it forms $C_{10}H_{10}N_2O_2$, [173°] (Griess, *B.* 2, 415). The latter is converted by boiling HCl into $C_8H_6N_2O_2$, [above 350°], which is probably $C_6H_4\left\langle\begin{matrix}NH.CO\\ |\\ O.NH\end{matrix}\right.$ since it can be formed by heating *o*-amido-benzoic acid with urea. It forms crystalline nitro- and amido-derivatives.

The compound $C_{10}H_{10}N_2O_2$ 'ethoxyl cyan-amidobenzoyl' is converted by alcoholic NH_3 at 100° into benzcreatinine (*q. v.*).

The compound $C_9H_5N_3O$ 'di-cyano-amido-benzoyl,' may be represented thus:

$C_6H_4\left\langle\begin{matrix}CO.N\\ \Vert\\ NH.C.CN\end{matrix}\right.$ (Griess, *B.* 18, 2417). This body gives the following reactions.—*a.* Strong NH_3Aq converts it into $C_6H_4\left\langle\begin{matrix}CO.N\\ \Vert\\ NH.C.CO.NH_2\end{matrix}\right.$, 'carboxamido-cyano-amido-benzoyl.'—*b.* Aqueous ammonium sulphide forms the corresponding $C_6H_4\left\langle\begin{matrix}CO.N\\ \Vert\\ NH.C.CS.NH_2\end{matrix}\right.$.—*c.* Baryta water forms $C_6H_4\left\langle\begin{matrix}CO.N\\ \Vert\\ NH.C.CO_2H\end{matrix}\right.$, 'carboxy-cyano-amido-benzoyl'; which is converted by dry distillation into $C_6H_4\left\langle\begin{matrix}CO.N\\ \Vert\\ NH.CH\end{matrix}\right.$ 'carbimido-amido-benzoyl.'—*d.* *m*-amido-benzoic acid produces the anhydride of di-phenyl-guanidine dicarboxylic acid, $C_6H_4\left\langle\begin{matrix}CO.N\\ \Vert\\ NH.C.NH.C_6H_4.CO_2H\end{matrix}\right.$.—*e.* *p*-phenylene-diamine produces the anhydride of amido-di-phenyl-guanidine carboxylic acid $C_6H_4\left\langle\begin{matrix}CO.N\\ \Vert\\ NH.C.NH.C_6H_4.NH_2\end{matrix}\right.$. All these bodies may be looked upon as derivatives of $C_6H_4\left\langle\begin{matrix}CH=N\\ |\\ N=CH\end{matrix}\right.$ which may be called *Quinazoline.*

Formyl derivative $C_6H_4(NHCHO)CO_2H\frac{1}{2}aq$. [168°]. Formed by heating isatoic or *o*-amido-

benzoic acid with formic acid (E. v. Meyer a. Bellmann, *J. pr.* [2] 33, 24). Hair-like needles; sol. alcohol, sl. sol. benzene.

Acetyl derivative $C_6H_4(NHAc)CO_2H$. [180°]. Formed by boiling anthranil (*q.v.*) with Ac_2O and treating the product with water (Friedländer a. Henriques, *B.* 15, 2105). Also by oxidation of (*Py.* 3)-methyl-quinoline by $KMnO_4$ (Doebner a. Miller, *B.* 15, 3075).

Preparation. — Acetyl-*o*-toluidine (1 g.) is oxidised by $KMnO_4$ (2 g.) dissolved in water (200 c.c.), the liquid being kept neutral by acetic acid (Bedson a. King, *C. J.* 37, 752).

Properties.—Lustrous leaflets (from water). Prisms (from HOAc). Trimetric, $a:b:c = \cdot982:1:2\cdot803$ (Fletcher).

Salts.—PbA'_2: flocculent pp.—AgA': needles.

Tests.—Solution of sodium salt gives with lead acetate a pp. sol. in acetic acid, with $CaCl_2$ a pp. only on adding alcohol.

Di-acetyl derivative $C_6H_4(NAc_2)CO_2H$. [220°].—AgA'.

Chloro-acetyl derivative $C_6H_4(NH.CO.CH_2Cl).CO_2H$. From acetyl derivative and PCl_5 (Jackson, *B.* 14, 888). Clumps.

Di-chloro-acetyl derivative $C_6H_4(NH.CO.CHCl_2).CO_2H$. [c. 173°]. Prepared like the preceding. Yellowish needles (from water).

Salt.—AgA'.

Benzoyl derivative $C_6H_4(NHBz).CO_2H$. [182°]. By BzCl; or by acting on benzoyl-*o*-toluidine with $KMnO_4Aq$ (Brückner, *A.* 205, 130). Long needles (from alcohol); insol. water.

Salts.—NaA' 4aq.—MgA'_2 4aq.—CaA'_2 3aq. —BaA'_2 3aq.

Oxaloxyl derivative v. CARBOXY-PHENYL-OXAMIC ACID.

Amide $C_6H_4(NH_2)CO.NH_2$. *Amido-benzamide.* [108°]. (300°). From NH_3 and isatoic acid (*q.v.*). White plates (from chloroform). Sl. sol. benzene and ether. Aqueous solution of (1 mol.) of its hydrochloride gives with $NaNO_2$ needles of $C_7H_5N_3O$, [213°]. This compound forms salts, *e.g.* $C_7H_4NaN_3O$, and a methyl ether, $C_7H_4MeN_3O$. The methyl ether, [123°], is also formed from the methylamide of *o*-amido-benzoic acid. The new substance is probably

$$C_6H_4\left\langle\begin{array}{l}CO.NH\\ \quad\;\;|\\ N=N\end{array}\right.$$ (Weddige a. Finger, *J. pr.* [2] 35, 262).

Acetyl-amido-benzamide $C_6H_4(NHAc)CONH_2$. [171°]. By Ac_2O. Needles. Forms salts with acids. If kept melted for some time it becomes solid, changing to the anhydro-compound, $C_6H_4\left\langle\begin{array}{l}NH.C.CH_3\\ \qquad\;\|\\ CO.N\end{array}\right.$ *Oxy-methyl-quinazoline* [228°]. Yellow silky needles (from alcohol). Soluble in hot water. Forms salts with acids.

Formyl-amido-benzamide $C_6H_4(NH.CHO)CONH_2$. [123°]. From dry formic acid and *o*-amido-benzamide. When heated this gives H_2O and an anhydro-compound $C_6H_4\left\langle\begin{array}{l}NH.C.H\\ \qquad\;\|\\ CO.N\end{array}\right.$ *Oxy-quinazoline* (A. Weddige, *J. pr.* [2] 31, 124).

Anilide $C_6H_4(NH_2)CO.NHPh$. [130°]. From aniline and isatoic acid. Needles (from benzene).

Phenyl-hydrazide $C_6H_4(NH_2)CO.NPh.NH_2$. [170°]. From isatoic acid and phenyl hydrazine in alcoholic solution at 70°. Yellow needles; sol. alcohol and chloroform, v. sl. sol. ether (E. v. Meyer a. Bellmann, *J. pr.* [2] 33, 21).

Hydroxylamide $C_6H_4(NH_2)CO.NH.OH$. [82°]. From isatoic acid (*q.v.*) and hydroxylamine solution (M. a. B.). Yellowish plates, sol. alcohol, ether, and chloroform.

o-Oxy-phenyl ether $C_6H_4(NH_2).CO_2.C_6H_4OH$. [136°]. From isatoic acid and pyrocatechin at 130° (M. a. B.). Needles (from water). Sol. alcohol and ether, sl. sol. water.

m-**Amido-benzoic acid** $C_6H_4(NH_2).CO_2H$ [1:3]. [173°–174°]. S.G. 1·51 at 4°; S. 2 in cold water, 4 in boiling water or alcohol.

Formation.—1. From *m*-nitro-benzoic acid by reduction (Zinin, *J. pr.* 36, 103; Gerland, *A.* 86, 143; 91, 185; Schiff, *A.* 101, 94; Beilstein a. Wilbrand, *A.* 128, 265).—2. From nitro-phthalic acid, Sn, and HCl (Faust, *Z.* [2] 5, 335).—3. From $C_6H_3Br(NH_2)CO_2H$ [4:3:1] by sodium-amalgam (Raveill, *A.* 222, 180).

Properties.—Crystalline clumps; sweet taste; may be sublimed. Aqueous solutions are browned by air.

Reactions.—1. HCl and $KClO_3$ form chloranil.

2. *Bromine* forms tri-bromo-amido-benzoic acid.

3. *Nitrous acid* forms *m*-di-AZO-benzoic acid.

4. The solution containing *m*-diazo-benzoic acid gives *m*-oxy-benzoic acid on heating.

5. Fusion with *urea* produces uramido-benzoic acid (*q. v.*).

6. Boiling with CS_2 and alcohol produces thio-carbonyl-di-amido-di-benzoic acid, $CS(NH.C_6H_4.CO_2H)_2$ (Merz a. Weith, *B.* 3, 812). This body is also formed by heating *m*-amido-benzoic acid with thio-urea; and, together with thio-carbimido-benzoic acid, by heating *m*-amido-benzoic acid with $CSCl_2$ (Rathke a. Schäfer, *A.* 169, 101). Thio-carbonyl-di-amido-di-benzoic acid does not melt below 300°; it is v. sl. sol. water, m. sol. alcohol or ether; converted by HgO, in presence of KOH (Griess, *A.* 172, 169), into carbonyl-di-amido-di-benzoic acid.

7. $CSCl_2$ produces the last-mentioned body and also thio-carbimido-benzoic acid $SCN.C_6H_4.CO_2H$. This may also be prepared by boiling thio-carbonyl-di-amido-benzoic acid with HCl. It is an amorphous insoluble powder, v. sl. sol. alcohol. Decomposes above 310°. It unites with aniline forming di-phenyl-thio-urea carboxylic acid, $PhNH.CS.NH.C_6H_4.CO_2H$ [191°]. This body is also formed by heating phenyl-thio-carbimide with *m*-amido-benzoic acid at 100° (Merz a. Weith, *B.* 3, 244). It forms slender needles (from water). V. sol. alcohol, and ether, sl. sol. benzene, and benzoline. $AgNO_3$ added to its alkaline solution gives a black pp. of Ag_2S; Fe_2Cl_6Aq gives a yellow pp.; $Pb(OAc)_2$ a white pp.; and $CuSO_4$ a green pp. (Aschan, *B.* 17, 430).

8. *Phosgene* produces carbonyl-di-amido-di-benzoic acid $CO(NH.C_6H_4.CO_2H)_2$ (Sarauw, *B.* 15, 44). This body is also formed by heat-

ing *m*-uramido-benzoic acid (*q. v.*) at 200° (Traube, *B.* 15, 2124). White powder; insol. water, alcohol, and benzene, sol. alkalis.—$BaA''3aq.$ — Ag_2A''.— PbA''. Its ether Et_2A'', [161°–162°], is formed by heating *m*-uramido-benzoic ether (Griess, *J. pr.* [2] 4, 294): needles (from dilute alcohol).

9. *Phenyl cyanate* forms on heating, phenyl-uramido-benzoic acid, $NPhH.CO.NH.C_6H_4.CO_2H$. [270°]. Concentric prisms, sol. alcohol, sl. sol. ether, insol. water (Kühn, *B.* 17, 2882).

10. Aqueous KCNO evaporated with *m*-amido-benzoic acid forms *thio-uramido-benzoic acid* $NH_2.CS.NH.C_6H_4.CO_2H$ (Arzruni, *B.* 4, 406).

11. Phenyl cyanate (*q.v.*) forms di-phenyl-urea carboxylic acid $CO_2H.C_6H_4.NH.CO.NPhH$.

12. PCl_5 converts amido-benzoic acid into a white powder which, when extracted with water, yields a solution greatly resembling solutions of albuminous substances. Thus if a little lime-water, NaCl, or $MgSO_4$, be added the liquid may be coagulated by heat, more especially if CO_2 be passed through the solution before heat is applied (Grimaux, *C.R.* 98, 231, 1336).

13. *Cyanogen gas* passed into an aqueous solution forms a dicyanide of amido-benzoic acid, and cyan-carbimid-amido-benzoic acid. Cyanogen passed into an alcoholic solution forms the dicyanide, guanido-di-benzoic acid, and ethoxy-carbimid-amido-benzoic acid.

The *di-cyanide* $(CN)_2NH_2.C_6H_4.CO_2H$, is a yellow, crystalline powder, insol. water, v. sl. sol. alcohol or ether. It does not form metallic salts (Griess, *B.* 11, 1985; Griess a. Leibius, *A.* 113, 332). On distillation it forms *m*-amido-benzonitrile (Griess, *B.* 1, 191; Hofmann, *B.* 1, 194). Boiling KOHAq or HCl converts it into benz-creatine (*q. v.*) (Griess, *B.* 3, 703).

Cyano-carbimidamido-benzoic acid $CO_2H.C_6H_4.NH.C(NH).CN$ forms elliptic plates, v. sl. sol. cold water, sol. acids and alkalis. It reacts as follows:—*a.* Nitrous acid converts it into cyano-carboxamido-benzoic acid, $CO_2H.C_6H_4.NH.CO.CN$. (Griess, *B.* 18, 2415), which forms white plates, insol. cold water, with sweetish taste; boiling water converts it into HCN, CO_2, and carboxy-amido-benzoic acid; dilute NH_3Aq forms uramido-benzoic acid.—*b.* Cold dilute HCl forms small prisms of carbox-amido-carbimidamido-benzoic acid $CO_2H.C_6H_4.NH.C(NH).CO.NH_2$; v. sol. hot water; its aurochloride, $HA'HAuCl_4 1\frac{1}{2}aq$, crystallises in needles (G.).—*c.* Cold aqueous di-methyl-amine forms $CO_2H.C_6H_4.NH.C(NH).C(NH).NMe_2$; six-sided plates, v. sol. hot water, sl. sol. cold water, converted by hot Na_2CO_3aq into *m*-carboxy-phenyl-oxamide NH_3 and NMe_2H.

Guanido-di-benzoic acid $NH:C(NH.C_6H_4.CO_2H)_2$ is also formed from thio-carbonyl-di-amido-di-benzoic acid, HgO, and NH_3 (Griess, *A.* 172, 172). It is crystalline. Salts.—BaA''.—$H_2A''HCl$.—$(H_2A''HCl)_2PtCl_4$.

Ethoxy-carbimidamido-benzoic acid, $EtO.C(NH).NH.C_6H_4.CO_2H 1\frac{1}{2}aq$ forms needles (from water), sol. alcohol, and ether; converted by alkalis into alcohol and uramido-benzoic acid; nitrous acid converts it into

Carboxy-amido-benzoic acid mono-ethyl ether $CO_2Et.NH.C_6H_4.CO_2H$ [189°]. This acid is also formed from amido-benzoic acid and $Cl.CO_2Et$. It crystallises in plates (from water). Salts.—$BaA'_2 2aq.$ — AgA' (Griess, *B.* 9, 796; Wachendorff, *B.* 11, 701). *Ether* EtA' [101°]; plates (from water). *Amide* $C_{10}H_{10}NO_3NH_2$. [158°] (W.).

Salts.—$HA'HCl$: prisms (Cahours, *A. Ch.* [3] 53, 322).—$(HA'HCl)_2PtCl_4$.—$HA'HClSnCl_2$.—$HA'HBr$.—$HA'HNO_3$.—$(HA')_2H_2SO_4aq.$ [225°]. $HA'H_3PO_4$ (Harbordt, *A.* 123, 290).—$BaA'_2 4aq.$ — $CaA'_2 3aq.$ — CuA'_2 — PbA'_2. Needles.—$MgA'_2 7aq.$—AgA'—NaA' (at 100°) (Voit, *A.* 99, 100).—$SrA'_2 2aq.$—ZnA'_2 (when dried at 100°).

Methyl ether.—MeA'. Oil (Chancel, *C. R.* 30, 751).

Ethyl ether.—EtA'. (294°). Liquid, sol. water; from *m*-nitro-benzoic ether. Salts: $EtA'HCl$. [185°]. (Müller, *B.* 19, 1493). — $(EtA'HCl)_2PtCl_4$.—$EtA'HNO_3$: prisms.

Acetyl derivative $C_6H_4(NHAc).CO_2H$. [245°]. *Formation.*—1. By AcCl or by HOAc at 140° (G. C. Foster, *C. J.* 13, 235).—2. From amido-benzoic acid (10 g.) and acetic ether (25 c.c.) at 150°. (Pellizzari, *A.* 232, 148).—3. From amido-benzoic acid and acetamide (P.), or Ac_2O (Kaiser, *B.* 18, 2946). *Properties.*—White powder, v. sol. hot alcohol, sl. sol. hot water, v. sl. sol. cold water and ether. Dissolves in Na_2HPO_4Aq, but re-ppd. by HOAc. May be sublimed. Salts.—$BaA'_2 3aq$: needles.—$CaA'_2 3aq.$—NaA' (at 120°).

Formyl derivative $C_6H_4(NH.CHO).CO_2H$. [225°] (Pellizzari, *G.* 15, 555).

Heptoyl derivative $C_6H_4(NH.C_7H_{13}O).CO_2H$. [202°] (P.)

Glycollyl derivative $C_6H_4(NH.CO.CH_2OH).CO_2H$. [212°]. Gives at 220° the anhydride $<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>N.C_6H_4.CO_2H$, [248°]. Acetyl derivative. [198°].

Lactyl derivative $CH_3.CH(OH).CO.NH.C_6H_4.CO_2H$. [162°]. Its anhydride melts at [243°] (P.).

Benzoyl-derivative $C_6H_4(NHBz)CO_2H$. [248°]. 1. From amido-benzoic acid and benzamide at 180° for 2 hours.—2. By boiling amido-benzoic acid (2 g.) with benzoic ether (4 c.c.) for 6 hours (Pellizzari, *A.* 232, 150).—3. From amido-benzoic acid and benzanilide at 230° (P.). Minute prisms (from alcohol). Soluble with ease in alcohol, less so in ether or water. Its Ca and Ba salts are soluble. Resolved by hot KOH into benzoic and amido-benzoic acids. *Anilide.*—$C_6H_4(NHBz)CONPhH$. [225°]. By heating $C_6H_4(NBzH)CO_2H$ with aniline for some hours.

Oxaloxyl derivative v. CARBOXY-PHENYL-OXAMIC ACID.

Succinyl-derivative $C_{11}H_9NO_4$ or

$CH_2.C=N.C_6H_4.CO_2H$.
| \ (?). [235°]. Formed by
$CH_2.CO.O$

melting succinoxyl-amido-benzoic acid, or by fusing succinic and amido-benzoic acids together (Muretow, *J. R.* 4, 295; Pellizzari, *B.* 18, 215). Needles (from alcohol). Sl. sol. cold water. Salts.—$BaA'_2 2aq.$—AgA'.

Succinoxyl derivative $C_{11}H_{11}NO_5$ *i.e.* $CO_2H.CH_2.CH_2.CO.NH.C_6H_4.CO_2H$. [230°]. From the preceding by boiling with water, baryta or ammonia (M.). Plates; m. sol. water. $BaA'' 1\frac{1}{2}aq.$

Succinyl-di-amido-di-benzoic acid

$C_{18}H_{16}N_2O_6$ *i.e.* $C_2H_4(CO.NH.C_6H_4.CO_2H)_2$. (?) [c. 300°]. Formed together with $CO_2Et.CH_2.CH_2.CO.NH.C_6H_4.CO_2H$ by heating alcoholic succinic ether with amido-benzoic acid (M.; P.). Also from succinyl-amido-benzoic acid, alcohol, and HCl (M.). White crystalline powder. Soluble in KOHAq. Salts: CaA″7aq. S. ·2.—BaA″ 5aq: needles.

Phthalyl derivative $C_{15}H_9NO_4$ *i.e.* $C_6H_4:C_2O_2:N.C_6H_4.CO_2H$. [282°]. Formed together with its ether by heating amido-benzoic acid with phthalic ether (Pellizzari, *B.* 18, 216). Ethyl ether: A′Et. [152°]: radiating needles.

Sebacyl derivative $C_{24}H_{28}N_2O_6$ *i.e.* $C_8H_{16}(CO.NH.C_6H_4.CO_2H)_2$. [275°]. Formed together with $CO_2Et.C_8H_{16}.CO.NH.C_6H_4.CO_2H$ by heating sebacic ether with amido-benzoic acid in alcoholic solution (P.). White powder, sl. sol. in most menstrua.

Amide $C_6H_4(NH_2).CO.NH_2$aq. *Amido-benzamide.* [75°]; when dry [above 100°]. From *m*-nitrobenzamide by ammonium sulphide (H. Schiff, *A.* 218, 185; Chancel, *A.* 72, 274).

Properties.—Large, yellow crystals. Unites with acids forming compounds:—$C_7H_8N_2OHCl$: needles.—$C_7H_8N_2OHNO_3$.—$(C_7H_8N_2OHCl)_2PtCl_4$.—$C_7H_8N_2OAgNO_3$: needles.

Reactions.—1. Aqueous solutions (even when very dilute) give with *fatty aldehydes* crystalline pps. of the form $R.CH(NH.C_6H_4.CO.NH_2)_2$. These are soluble in alcohol, but give with HNO_3 containing CrO_3 a violet colour. They differ from original amido-benzamides in being no longer basic and in giving no coloured compounds with furfurol solution.—2. Aqueous *salicylic aldehyde* gives yellowish needles of $C_6H_4(OH).CH:N.C_6H_4NH_2$. [186°]. V. e. sol. alcohol or warm water. This compound, *o*-oxy-benzylidene-amido-benzamide, boiled with benzoic aldehyde forms a product $C_{35}H_{28}N_4O_3$, insoluble in water, alcohol, ether, toluene, chloroform or CS_2, but may be crystallised from phenol (2 vols.) and alcohol (1 vol.). It may be considered to be an anhydride of

$C_6H_5.CH(NH.CO.C_6H_4.N:CH.C_6H_4.OH)_2$.

Boiled with Ac_2O it takes up 1 molecule of Ac_2O forming small needles. Dilute aqueous NH_3 reproduces the compound $C_{35}H_{28}N_4O_3$. — 3. *Helicin* (2 pts.), *m*-amido-benzamide (1 pt.), and water (10 pts.) form yellowish plates of a glucoside of *o*-oxy-benzylidene-amido-benzamide [113°]: $NH_2.CO.C_6H_4.N:CH.C_6H_4.O.C_6H_{11}O_5$ 2aq. 4. Boiled with an alcoholic solution of *isatin* it forms a crystalline powder [c. 280°] of isat-amido-benzamide:

$NH{<}{\begin{smallmatrix}C_6H_4\\CO\end{smallmatrix}}{>}C:N.C_6H_4.CO.NH_2$. The compounds $NH_2.CO.C_6H_4.N:X$ derived from aldehydes and amido-benzamide are decomposed by heating with aniline into amido-benzamide and PhN:X (Schiff, *G.* 13, 113; *A.* 218, 185).

Phthalyl-amido-benzamide

$NH_2.CO.C_6H_4.N:\underset{|}{C}.C_6H_4$
$\quad\quad\quad\quad\quad O.CO$ [240°–241°]. Got by fusing *m*-amido-benzamide with phthalic anhydride. Bundles of slender needles (from alcohol). V. sl. sol. water. Heated with aniline gives phenyl-phthalimide and amido-benzamide (H. Schiff, *A.* 218, 194).

m-Amido-benzamidoxim

$C_6H_4(NH_2).C(NH_2):NOH$. A crystalline solid; formed by reduction of *m*-nitro-benz-amidoxim with $SnCl_2$. Salt.—B′HCl; prisms (Schöpff, *B.* 18, 2472).

Anilide $NH_2.C_6H_4.CO.NPhH$. *Amido-benzanilide.* [129°]. (P.); [114°] (E. a. V.). Formed by heating *m*-amido-benzoic acid with aniline (Piutti, *B.* 16, 1321) or by reducing *m*-nitro-benzanilide (Engler a. Volkhausen, *B.* 8, 35).—Silvery scales (P.) or long needles (from water, E. a. V.). Heated with aniline at 200° it forms two isomerides, $(C_7H_5NO)_n$, one soluble in alcohol, [225°], called 'amido-benzoïde,' and the other an insoluble powder (Piutti, *G.* 13, 339). Salts: $C_{13}H_{12}N_2OHCl$.—$(C_{13}H_{12}N_2O)_2H_2SO_4$

p-**Amido-benzoic acid** $C_6H_4(NH_2)CO_2H$. [186°–187°]. *Amido-dracylic acid.*

Formation.—1. By reducing *p*-nitro-benzoic acid (G. Fischer, *A.* 127, 142; Wilbrand a. Beilstein, *A.* 128, 264). — 2. By boiling its succinoxyl-derivative with HCl (Michael, *B.* 10, 576).

Preparation.—50 pts. of acetyl-*p*-toluidine is suspended in about 2000 pts. of boiling water and oxidised by slowly adding 200 pts. of finely powdered $KMnO_4$. The solution is filtered from MnO_2, the acetamido-benzoic acid ppd. by HCl, and saponified by boiling for an hour with strong HCl (Kaiser, *B.* 18, 2942).

Properties.—Long white needles, not coloured by moist air. When heated with urea it forms $CO(NH.C_6H_4.CO_2H)_2$ (Griess, *J. pr.* [2] 5, 370).

Salts.—BaA'_2: shining laminæ, sol. water. —A′.Pb.OAc, ppd. by $Pb(OAc)_2Aq$ (Ladenburg, *B.* 6, 130). — $(HA')_2H_2SO_4$. — The *copper-salt* is a dark-green pp. (Geitner a. Beilstein, *A.* 139, 1).

Acetyl derivative $C_6H_4(NHAc).CO_2H$. [250°]. Formed from acetyl-*p*-toluidine by $KMnO_4$ (Hofmann, *B.* 9, 1302). Needles, sl. sol. water. Salt: AgA′.

Benzoyl derivative $C_6H_4(NHBz)CO_2H$. [278°]. From benzoyl-*p*-toluidine, CrO_3, and HOAc (Brückner, *A.* 205, 127).—Small needles (from alcohol). Salts.—BaA'_2.—CaA'_2.

Succinoxyl-derivative

$CO_2H.CH_2.CH_2.CO.NH.C_6H_4.CO_2H$. [226°]. From *p*-tolyl-succinimide and dilute $KMnO_4$ (Michael, *B.* 8, 577). Yellowish needles, sl. sol. cold water. Salt.—$C_{11}H_{10}NO_5Ag$.

Amide $C_6H_4(NH_2).CO.NH_2$. [179°]. Formed by reducing *p*-nitro-benzamide (Beilstein a. Reichenbach, *A.* 132, 144). Yellow crystals, sl. sol. water.

Di-amido-benzoic acids $C_7H_8N_2O_2$ (Griess, *A.* 154, 325; *B.* 2, 47, 434; 5, 192; 7, 1227; 17, 603; *Pr.* 20, 168; Wurster a. Ambühl, *B.* 7, 213; V. Meyer a. Wurster, *B.* 5, 635; *A.* 171, 62). These acids can be formed by reducing the corresponding di-nitro-, or nitro-amido-, benzoic acids. They are soluble in water, combine both with acids and bases, and split up, when distilled with baryta, into CO_2 and phenylene-diamine.

Nitrous acid converts the (*a*) acid into amido-di-azo-benzoic acid, $C_6H_3(NH_2){<}{\begin{smallmatrix}CO\\N_2\end{smallmatrix}}{>}O$; the (*β*) and (*γ*) acids are converted by it into azimido-benzoic acids, $HN_3:C_6H_3.CO_2H$, while the symmetrical acid becomes tri-amido-azo-ben-

-soic acid $C_6H_3(NH_2)(CO_2H).N_2.C_6H_2(NH_2)_2CO_2H$ v. Azo compounds.

s-di-amido-benzoic acid
$C_6H_3(CO_2H)(NH_2)_2$ aq [1:3:5]. [228°]. S. 1·1 at 8° (Voit, *A.* 99, 106; Hübner, *A.* 222, 85). Colourless needles, neutral to litmus; loses aq at 110°. Very dilute solutions are turned yellow by HNO_2.

Salts.—HA'2HCl: needles.—$HA'H_2SO_4$.—S. 1·05 at 11°.—BaA'_2 1½aq.—AgA' 2aq.

Amide $C_6H_3(CONH_2)(NH_2)_2$ *di-amido-benzamide.* [177°] (V.); [183°] (M.). Needles (Muretow, *Z.* [2] 6, 642). Salt.—$C_7H_9N_3O$ 2HCl: silky needles. *Di-acetyl-derivative* $C_6H_3(CONAc_2)(NH_2)_2$ 2aq. [Above 270°]. Thin needles, sl. sol. cold water (M.).

(a)-di-amido-benzoic acid
$C_6H_3(CO_2H)(NH_2)_2$. [1:2:5]. Formed also from nitro-isatoic acid by Sn and HCl (Kolbe, *J. pr.* [2] 30, 480). Very small prisms (from water). V. sl. sol. alcohol, ether, and boiling water (G.). The free acid turns blue in air.

Salts.—$HA'H_2SO_4$: needles, v. sl. sol. water.—HA'2HCl (K.).

(β)-di-amido-benzoic acid
$C_6H_3(CO_2H)(NH_2)_2$ [1:3:4]. [211°] (Salkowski, *A.* 173, 57; Griess, *B.* 5, 856). Plates. Sl. sol. cold water.

Salts.—$HA'H_2SO_4$: plates; v. sl. sol. hot water.—HA'HCl 1½aq.

(γ)-di-amido-benzoic acid
$C_6H_3(CO_2H)(NH_2)_2$ [1:2:3]. Long needles.

Salt.—$(HA')_2H_2SO_4$ 1½aq: six-sided tables or columns, v. sl. sol. water; Fe_2Cl_6 colours its solution brownish-red.

Tri-amido-benzoic acids $C_7H_9N_3O_2$.

I. $C_6H_2(CO_2H)(NH_2)_3$ ½aq [1:3:4:5]. From di-nitro-amido-benzoic (or chrysanisic) acid (Salkowski, *A.* 163, 12).

Needles (from water). Sl. sol. cold water, v. sl. sol. alcohol, and ether; solution is acid. Heat splits it up into CO_2 and tri-amido-benzene. Its solutions give a brown pp. with Fe_2Cl_6.

Salts.—HA'2HCl: silver-grey needles.—$HA'(HCl)_2SnCl_2$ 3½aq: monoclinic.—$HA'H_2SO_4$aq: sl. sol. hot water.—$HA'2HNO_3$.—CaA'_2.—ZnA'_2 6aq.

II. $C_6H_2(CO_2H)(NH_2)_3$ [1:2:3:5]. Formed by reduction of *p*-sulpho-benzene-azo-*s*-di-amido-benzoic acid (Griess, *B.* 15, 2200).

Colourless crystals; v. sol. hot water; sl. sol. alcohol, insol. ether. Very readily oxidised.

Salt.—$HA'H_2SO_4$; small white needles, v. sl. sol. water, insol. alcohol.

References.—Chloro-, Bromo-, Iodo-, Nitro-, and Methyl-, amido-benzoic acids and amido-sulpho-benzoic acid.

AMIDO-BENZOIC ALDEHYDES C_7H_7NO.

***o*-Amido-benzoic aldehyde** $C_6H_4(NH_2)$.CHO [1:2]. [40°]. Formed by oxidising its oxim with Fe_2Cl_6 (Gabriel, *B.* 15, 2004).

Preparation.—*o*-nitro-benzaldehyde (3 g.) is digested with $FeSO_4$ (50 g.) and NH_3 at 100° (Friedländer a. Göhring, *B.* 17, 456).

Properties.—Silvery plates; volatile with steam; may be distilled. V. sol. alcohol, ether. and benzene, sl. sol. water, insol. light petroleum.

Salt.—$B'_2H_2PtCl_6$: large yellow prisms (from HClAq).

Reactions.—Very stable towards alkalis, but condensed by acids to $C_{14}H_{12}N_2O$, which is probably $C_6H_4(NH_2)$.CH:N.C_6H_4.CHO; this forms small colourless needles [189°], is not volatile with steam, and possesses only weak basic properties; NH_3Aq, conc. HClAq, and hot dilute HClAq reconvert it into amido-benzaldehyde.

Acetyl derivative C_6H_4(NHAc).CHO. [71°]. White needles (Friedländer, *B.* 15, 2572).

Oxim $C_6H_4(NH_2)$CH.NOH. [133°]. Formed by reducing *o*-nitro-benzaldoxim (Gabriel, *B.* 14, 2338; 15, 3057; 16, 517). Needles; may be sublimed. Sol. alcohol and ether, sl. sol. water and benzene. Its methyl derivative $C_6H_4(NH_2)$CH:NOMe melts at [58°] (R. Meyer, *C. C.* 1885, 516). Its acetyl-methyl derivative C_6H_4(NHAc)CH:NOMe [109°], and its di-acetyl derivative C_6H_4(NHAc)CH:NOAc [128°] are crystalline, insol. acids and alkalis.

***m*-Amido-benzoic aldehyde.**

Oxim $C_6H_4(NH_2)$.CH:NOH. [88°]. Formed by reducing *m*-nitro-benzaldoxim with $FeSO_4$ and NH_3 (Gabriel, *B.* 16, 1997). White felted needles. Sol. alcohol, ether, and hot benzene, sl. sol. cold benzene, and benzoline. Dissolves in acids and alkalis. Salt: $B'_2H_2PtCl_6$; orange yellow tables.

***p*-Amido-benzoic aldehyde** $C_6H_4(NH_2)$.CHO [1:4]. [71°]. Formed by action of acids on its oxim. Flat plates, sol. water. With acids it forms red salts.

Acetyl derivative C_6H_4(NHAc).CHO. [155°]. Long white needles.

Oxim. — $C_6H_4(NH_2)$.CH:NOH. [124°]. Formed by reducing the oxim of *p*-nitro-benzoic aldehyde by ammonium sulphide (Gabriel a. Herzberg, *B.* 16, 2000). Flat yellow crystals, sol. water, alcohol, ether, acids, and alkalis. Its acid solution is resolved, even in the cold, into hydroxylamine and *p*-amido-benzoic-aldehyde. Acetyl derivative C_6H_4(NHAc).CH:NOH. [206°]. White plates.

AMIDO-BENZONITRILES $C_7H_6N_2$.

***o*-Amido-benzonitrile** $NH_2.C_6H_4$.CN [1:2]. [103°]. By reduction of *o*-nitro-benzonitrile (Baerthlein, *B.* 10, 1714). Needles; v. sol. water, alcohol, and ether.

***m*-Amido-benzonitrile** $NH_2.C_6H_4$.CN [1:3]. [52°]; (290°).

Formation.—1. By reducing *m*-nitro-benzonitrile (Hofmann, *Z.* [2] 4, 726; Fricke, *B.* 7, 1321).—2. By distilling the dicyanide of *m*-amido-benzoic acid (*v.* p. 157, *l.* 32) (Griess, *B.* 1, 191).—3. By heating *m*-uramido-benzoic acid (*q. v.*) with P_2O_5 (Griess, *B.* 8, 861).

Properties.—Needles or prisms, sl. sol. water, v. e. sol. alcohol.

Salts.—B'HCl.—$B'_2H_2PtCl_6$: four-sided tables.—$B'AgNO_3$: white laminæ.

***p*-Amido-benzonitrile** $NH_2.C_6H_4$.CN [1:4]. [110°] (F.); [74°] (E.). Formed by reducing *p*-nitro-benzonitrile (Engler, *A.* 149, 302), or by distilling *p*-uramido-benzoic acid (F.).—Needles, v. sol. alcohol, ether, and boiling water.—B'HCl.—$B'_2H_2PtCl_6$: needles.

AMIDO-BENZOPHENONES $C_{13}H_{11}NO$.
Amido-di-phenyl-ketones.

***o*-Amido-benzophenone** $Bz.C_6H_4.NH_2$ [1:2]. [106°]. Formed by reducing *o*-nitro-benzophenone with Sn and HCl (Geigy a. Koenigs, *B.*

187 2408). Yellow plates, or thick crystals, v. sol. dilute acids, alcohol, and ether.

***m*-Amido-benzophenone** $Bz.C_6H_4.NH_2$ [1:3]. [89°]. From *m*-nitro-benzophenone and $SnCl_2$ (G. a. K.).—Yellow felted needles, sol. alcohol, and ether, sl. sol. water.—B′HCl: [187°]; long needles.

***p*-Amido-benzophenone** $Bz.C_6H_4.NH_2$ [1:4]. [124°]. *Benzo-aniline.* Prepared by boiling its phthalyl derivative with alcoholic KOH (Doebner, *B.* 13, 1011; Doebner a. Weiss, *B.* 14, 1836). Colourless plates, v. sol. alcohol, ether, and glacial HOAc, sl. sol. cold water. Nitrous acid converts it into *p*-oxy-benzophenone. On fusion with $ZnCl_2$ it loses H_2O forming a compound of the formula $C_{13}H_9N$. The latter is a very stable indifferent substance, crystallising in glistening plates [118°], and distils undecomposed at a high temperature; it is soluble in alcohol, ether, &c., sparingly in hot water, insoluble in cold.

Salts.—$B'_2H_2SO_4$: long sparingly soluble needles.—B′HCl, $B'_2H_2C_2O_4$, and $B'HNO_3$ are more soluble.—$(B'HCl)_2PtCl_4$: yellow needles; sl. sol. cold water.

Acetyl derivative $C_6H_5.CO.C_6H_4.NHAc$. [153°]. Long needles. Sol. alcohol, ether, acetic acid and benzene; insol. water.

Benzoyl derivative $C_6H_5.CO.C_6H_4.NHBz$. [152°]. Plates, sol. hot alcohol, sl. sol. cold alcohol, insol. water.

Phthalyl derivative $C_{21}H_{13}NO_3$ *i.e.* $C_6H_5.CO.C_6H_4.N(C_2O_2C_6H_4)$. [183°]. Prepared by the action of BzCl on phthalanil in presence of $ZnCl_2$. Large needles or plates, insol. water, sl. sol. alcohol or ether.

(α)-Di-amido-benzophenone $C_{13}H_8O(NH_2)_2$. [172°]. Prepared by reducing (α)-di-nitro-benzophenone, [190°] itself got from di-nitro-di-phenyl-methane. [183°] (Staedel a. Sauer, *B.* 11, 1747; *A.* 218, 344). White needles.

B″2HCl: large tables.—$B''2HClSnCl_2$.—$B''H_2SO_4$.

(β)-Di-amido-benzophenone $C_{13}H_{12}N_2O$. [165°]. *Flavine.*—From di-nitro-benzophenone [149°] by reduction (Chancel a. Laurent, *A.* 72, 281; Prætorius, *B.* 11, 744).—Slender yellow needles (from water).

Salts: $B''H_2Sn_2Cl_6$; plates.—$B''H_2PtCl_6$.

Acetyl derivative $C_{13}H_8O(NHAc)_2$: needles, [227°].

Oxim $(C_6H_4.NH_2)_2C:NOH$: [178°]; crystalline.

Phenyl-hydrazide $(C_6H_4.NH_2)_2C:N_2HPh$: [183°]; yellowish needles (from hot alcohol). (Münchmeyer, *B.* 20, 511).

(γ)-Di-amido-benzophenone, $C_{13}H_8O(NH_2)_2$ [181°]. From the di-nitro-benzophenone [190°] obtained from benzophenone (Staedel, *A.* 218, 349).—Glittering tablets.

Salt.—B″2HCl.

Acetyl derivative.—$C_{13}H_8O(NAcH)_2$. [167°]. Tables; insol. water; v. sol. alcohol.

AMIDO-BENZOYL-CARBAMIDE *v.* UREA.

AMIDO-BENZOYL-FORMIC ACID *v.* AMIDO-PHENYL-GLYOXYLIC ACID.

AMIDO-BENZOYL-GLYOXYLIC ACID *v.* QUINISATIC ACID.

AMIDO-BENZOYL-UREA *v.* UREA.

DI-AMIDO-DI-BENZYL $C_{14}H_{16}N_2$ *i.e.* $NH_2.C_6H_4.CH_2.CH_2.C_6H_4.NH_2$. [132°]. From the (*p*) nitro-compound (*q. v.*) by reduction.—Colourless scales (from hot water), v. sl. sol. cold water, v. sol. alcohol; may be sublimed.

Salts: B″2HCl.—$B''H_2PtCl_6$.—$B''H_2SO_4$.—$B''H_2C_2O_4$.—$B''(H_2C_2O_4)_2$ 3aq (Fittig a. Stelling, *A.* 137, 262).

AMIDO-BENZYL ALCOHOL C_7H_9NO *i.e.* $NH_2.C_6H_4.CH_2OH$. [1:2]. [82°]. Prepared by the action of zinc dust and HCl upon *o*-nitro-benzyl-alcohol, *o*-nitro-benzoic aldehyde, or anthranil (Friedländer a. Henriques, *B.* 15, 2109). White needles, insol. light petroleum; slightly volatile with steam.

AMIDO-BENZYL-AMINE $C_7H_{10}N_2$ *i.e.* $NH_2.C_6H_4.CH_2NH_2$ [1:4]. (269°). S.G. $\frac{20}{}$ 1·08. *Benzylene diamine.* From acetyl-*p*-nitro-benzyl-amine, Sn, and HCl: the Ac being split off in the operation (Amsel a. Hofmann, *B.* 19, 1287).—Colourless liquid, v. sol. water and alcohol, insol. ether; alkaline, absorbing CO_2 from the air.

Salts.—B″2HCl: needles, v. sol. water.—$B''_2(HCl)_4PtCl_4$: flat needles. The *nitrate* and *oxalate* crystallise in long white needles. $AgNO_3$ forms a double salt in large plates.

Di-amido-di-benzyl-amine $C_{14}H_{17}N_3$ *i.e.* $(NH_2.C_6H_4.CH_2)_2NH$. [106°]. From the nitro compound (Strakosch, *B.* 6, 1060). Needles or plates; may be distilled, but not volatile with steam. Salts.—B‴3HCl.—$B'''(HCl)_3PtCl_4$.

Tri-amido-tri-benzyl-amine $C_{21}H_{24}N_4$ *i.e.* $(NH_2.C_6H_4.CH_2)_3N$. [136°]. From the nitro compound (S.).—Octahedra (from alcohol); not volatile with steam. Insol. water, v. sol. hot alcohol. Reduced by Sn and HCl to *p*-toluidine and the preceding body.

AMIDO-BENZYL-ANILINE $C_{13}H_{14}N_2$ *i.e.* $NH_2.C_6H_4.CH_2.NPhH$. [88°]. From the nitro-compound by NH_3 and H_2S at 100° (Strakosch, *B.* 6, 1063).—Scales, v. sol. alcohol, ether, and benzene, not volatile with steam. Salt.—B″2HCl; v. sol. water, less so in HClAq.

AMIDO-BENZYL-BENZENE *v.* AMIDO-DI-PHENYL-METHANE.

AMIDO-BENZYL CYANIDE *v.* NITRILE OF AMIDO-PHENYL-ACETIC ACID.

DI-*p*-AMIDO-DI-BENZYL-MALONIC-ETHYL-ETHER $(C_6H_4(\overset{(4)}{NH_2}).\overset{(1)}{CH_2})_2:C(CO_2Et)$. Obtained by reduction of di-nitro-di-benzyl-malonic ether with $SnCl_2$.

Salts:—$(A''Et_2)H_2Cl_2$: [230°], easily soluble needles.—$(A''Et_2)H_2SO_4$: scales.—$(A''Et_2)H_2C_2O_4$: glistening yellow scales.—$(A''Et_2)H_2Cl_2PtCl_4$: reddish-brown plates (Lellmann a. Schleich, *B.* 20, 436).

AMIDO-BENZYL-PHENOL $C_{13}H_{13}NO$ *i.e.* $C_6H_5.CH_2.C_6H_3(NH_2)(OH)$. [1:3:4]. From the nitro-compound. Scales (Rennie, *C. J.* 41, 221).

DI-AMIDO-BENZYL-TOLUENE $C_{14}H_{16}N_2$. A crystalline powder, obtained by reducing di-nitro-*p*-benzyl-toluene (*q. v.*) (Zincke, *B.* 5, 684). Salts.—B″2HCl.—$B''H_2SO_4$.

AMIDO-BROMO-COMPOUNDS *v.* BROMO-AMIDO-COMPOUNDS.

AMIDO-BRUCINE *v.* BRUCINE.

AMIDO-BUTYL-BENZENE *v.* AMIDO-PHENYL-BUTANE.

AMIDO-BUTYRIC ACIDS $C_4H_9NO_2$.

α-Amido-*n*-butyric acid $CH_3.CH_2.CH(NH_2).CO_2H$. S. 3 at 15°; S. (alcohol) ·18 at 80°. From α-bromo-butyric acid and NH_3Aq (R. Schneider, *A. Suppl.* 2, 71).—Stellate groups of small

laminæ or needles (from alcohol); neutral; sweet taste; insol. ether.

Salts.—HA'HCl; v. sol. water.—HA'HNO$_3$; fern-like groups of silky needles.—(HA')$_2$H$_2$SO$_4$.—HOPb.A'.—AgA'.

β-Amido-*n*-butyric acid

$CH_3.CH(NH_2).CH_2.CO_2H$.

Amide $CH_3.CH(NH_2).CH_2.CO.NH_2$. An amorphous mass, obtained by the action of alcoholic NH_3 on β-chloro-*n*-butyric ether (Balbiano, *G.* 10, 137; *B.* 13, 312). Its platino-chloride crystallises in orange tables, sl. sol. alcohol.

α-Amido-*iso*-butyric acid $CMe_2(NH_2).CO_2H$.

Formation.—From acetonyl-urea and fuming HCl at 160° (Urech, *A.* 164, 268).—2. From di-acetonamine (Heintz, *A.* 192, 343; 198, 46).

Preparation.—The acetone cyanhydrin, obtained by the action of dilute HCN on acetone, is heated with alcoholic NH_3 at 60°, and the product saponified (Tiemann a. Friedländer, *B.* 14, 1971).

Properties.—Plates or tables, v. sol. water, sl. sol. alcohol, insol. ether; sublimes at about 220°.

Salts.—BaA'$_2$ 2aq: needles.—MgA'$_2$: thick prisms.—CuA'$_2$: plates, giving a violet solution.—AgA': needles, sol. water.—HA'HCl 2aq.—HA'HCl.

Nitrile.—$CMe_2NH_2.CN$. The product of the action of alcoholic NH_3 on acetone-cyanhydrin (*vid. sup.*).

AMIDO-CAMPHOR *v.* CAMPHOR.

AMIDO-CAMPHORIC ACID *v.* CAMPHORIC ACID.

AMIDO-CAPROIC ACID *v.* LEUCINE, and AMIDO-HEXOIC ACID.

AMIDO-CAPRYL-BENZENE *v.* AMIDO-PHENYL-OCTANE.

AMIDO-CAPRYLIC ACID *v.* AMIDO-OCTOIC ACID.

AMIDO-CARBOSTYRIL $C_9H_8N_2O$ *i.e.*

$C_6H_4{<}{}^{CH:CH}_{N(NH_2)}{>}CO$. [127°]. *Anhydride of hydrazido-cinnamic acid; Oxy-amido-quinoline; Amido-pseudo-carbostyril.* Prepared by converting diazo-cinnamic acid by Na_2SO_3 into $SO_3Na.N_2.C_6H_4.CH:CH.CO_2H$, then reducing this substance by acetic acid and zinc dust to $SO_3Na.NH.NH.C_6H_4.CH:CH.CO_2H$, boiling this with HCl and then adding KOH (Fischer a. Kuzel, *A.* 221, 278).

Properties.—Slender needles; may be sublimed; sol. alcohol, ether, and hot water. It forms salts with acids.

Reactions.—1. Does not reduce alkaline copper or silver solutions.—2. Nitrous acid converts it, even in the cold, into carbostyril.

γ-Amido-carbostyril. From carbostyril by nitration and reduction (Friedländer a. Lazarus, *A.* 229, 246). Yellow plates (from glacial HOAc). Does not melt below 320°.

Methyl derivative $C_9H_5N(NH_2)(OMe)$. [103°], *amido-*(Py. 3)*-methoxy-quinoline.* Formed from the nitro-compound by $SnCl_2$ (Feer a. Koenigs, *B.* 18, 2397).—Silvery plates; v. sol. alcohol and ether; m. sol. warm water. Its ethereal solution has a bluish fluorescence. $KMnO_4$ oxidises it to methoxy-quinolinic acid [140°]. Dilute HCl at 120° forms (γ)-amido carbostyril.

See also OXY-AMIDO-QUINOLINE.

AMIDO-CHROMATE OF POTASSIUM *v.* ***Amido-chromates.*** under CHROMIUM, ACIDS OF.

AMIDO-CHRYSANISIC ACID *v.* NITRO-DI-AMIDO-BENZOIC ACID.

AMIDO-CINNAMIC ACIDS $C_9H_9NO_2$.

α-Amido-cinnamic acid

$C_6H_5.CH:C(NH_2).CO_2H$. Obtained by saponifying its benzoyl derivative.—Silvery plates, decomposing at 240°–250° (Plöchl, *B.* 17, 1619).

Salts.—CuA'$_2$ 2aq: small blue prisms.—(HA')$_2$HCl: flat n[illegible]. sol. cold water and alcohol.

Benzoyl derivative

$C_6H_5.CH:C(NHBz).CO_2H$ [131°]. Formed by heating an acetic acid solution of benzoyl-di-amido-hydrocinnamic lactam $\begin{matrix} C_6H_5.CH.CH(NHBz). \\ \quad\quad | \quad\quad | \\ \quad\quad NH.CO \end{matrix}$

Needles or prisms; sol. alcohol, ether, and hot water.

***o*-Amido-cinnamic acid**

$NH_2.C_6H_4.CH:CH.CO_2H$ [1:2]. [159°].

Preparation.—From *o*-nitro-cinnamic acid (150 g.), crystallised baryta (2100 g.), water (30 litres), and ferrous sulphate (1400 g.), by heating two hours at 100° (Fischer a. Kuzel, *A.* 221, 266; Tiemann a. Opermann, *B.* 13, 2061). Ammonia may be used in place of baryta (Gabriel, *B.* 15, 2294; Friedländer, *A.* 229, 241).

Properties.—Yellow needles; sol. alcohol, ether, and hot water, sl. sol. cold water. Dissolves in aqueous alkalis and acids.

Salts.—HA'HCl; prisms.—BaA'$_2$; prisms.

Ether.—EtA' [78°]. May be distilled. Yellow needles, with yellowish-green fluorescence. Its hydrochloride is sparingly soluble in excess of conc. HCl; its acetyl derivative, [137°], forms white needles, which may be distilled (Friedländer a. Weinberg, *B.* 15, 1422).

Ethyl derivative

$C_6H_4(NHEt).CH:CH.CO_2H$. From the acid (60 g.), KOH (96 c.c. of 20 p.c. solution), alcohol (240 g.), and EtI (60 g.), by boiling (F. a. K.).

Reactions.—1. Long boiling with HClAq forms carbostyril.—2. $ZnSO_4Aq$ gives a crystalline pp.—3. $AgNO_3Aq$ gives a white pp.—4. $CuSO_4Aq$ gives a light green pp.—5. $Pb(OAc)_2Aq$ gives a yellow pp.

***m*-Amido-cinnamic acid**

$C_6H_4(NH_2).CH:CH.CO_2H$ [1:3]. [181°]. The preparation is similar to that of the *o*-compound.

Properties.—Long yellow needles; sol. alcohol, ether, and hot water. Dissolves in aqueous acids and alkalis.

Reactions.—1. $CuSO_4Aq$ gives a dull green pp.—2, 3, same as above.—4. $Pb(OAc)_2Aq$ gives a white pp. sol. hot water (T. a. O.).

Salts.—HA'HCl: plates.—(HA'HCl)$_2$PtCl$_4$.—HA'HNO$_3$: slender needles.—BaA'$_2$ 2aq: plates.

***p*-Amido-cinnamic acid**

$C_6H_4(NH_2).CH:CH.CO_2H$ [1:4]. [176°]. Prepared by reducing *p*-nitro-cinnamic ether in alcoholic solution with tin and HCl; yield: 75 p.c. (Miller a. Kinkelin, *B.* 18, 3234). Slender yellow needles, sol. water, alcohol, and ether. Dissolves in aqueous alkalis and acids.

Reactions.—1. $CuSO_4Aq$ a brown pp.—2, 3, and 4, the same as for the *m*-compound.

Salts.—HA'HCl.—(HA'HCl)$_2$PtCl$_4$.

Acetyl derivative [260°]. Long needles, sol. hot alcohol, sl. sol. water, v. sl. sol. ether and benzene (Gabriel a. Herzberg, *B.* 16, 2041).

Di-amido-cinnamic acid $C_6H_3(NH_2)_2.CH:CH.CO_2H$. [168°]. Formed by reducing (3:4:1)-nitro-amido-cinnamic acid (Gabriel a. Herzberg, *B.* 16, 2042). Yellow needles, sol. hot alcohol, and water, insol. ether, benzene, and benzoline.

AMIDO-COMENIC ACID *v.* COMENIC ACID.

AMIDO-COUMARIN $C_9H_7NO_2$. [168°–170°]. From nitro-coumarin (*q. v.*).—Needles, v. sl. sol. cold water, v. sol. hot water. Salt.—$(B'HCl)_2PtCl_4$ (Frapolli a. Chiozza, *A.* 95, 253).

AMIDO-CRESOL C_7H_9NO. Mol. w. 142. Ten amido-cresols are indicated by theory: four derived from *ortho-*, four from *meta-*, and two from *para-cresol*. The amido-cresols are readily soluble in alcohol and in ether, sparingly so in water. They dissolve in acids and in alkalis. They are formed by reducing nitro-cresols, or from nitro-toluidines by the diazo reaction.

Amido-*o*-cresols $C_6H_3Me(OH)(NH_2)$ [1:2:x].

Amido-*o*-cresol $x=3$. From nitro-*o*-cresol [69°] (Hofmann a. Miller, *B.* 14, 570; Zincke a. Hebebrand, *A.* 226, 72).

Reaction.—1. When heated with quinone, it forms a red crystalline *Base*, $C_{28}H_{26}N_4O_{11}$ [285°], v. sl. sol. alcohol, sol. acids; its acetyl derivative, $C_{28}H_{24}Ac_2N_4O_4$, forms orange needles (from dry HOAc).—2. Heated with formic acid it forms a methenyl compound: $C_6H_3Me\langle{}^{N}_{O}\rangle CH$, [39°], (200°).

Methyl ether $C_6H_3Me(OMe)(NH_2)$. (223°).

Amido-*o*-cresol $x=4$. [161°]. From nitro-*o*-cresol [108°] (Nölting a. Collin, *B.* 17, 270). Also from acetyl-tolylene-di-amine, $C_6H_3Me(NH_2)(NHAc)$ [1:2:4] (Wallach, *B.* 15, 2831). Colourless plates or needles. Salt.—B'HCl: glittering plates, which sublime as needles.

Acetyl derivatives

$C_6H_3Me(OH)(NHAc)$. [225°]; sol. KOHAq.—$C_6H_3Me(OAc)(NAcH)$. [133°] (Maassen, *B.* 17, 608; Wallach, *A.* 235, 250).

Amido-*o*-cresol $x=5$. [175°].

Formation. — 1. From nitro-*o*-cresol [85°] (Hirsch, *B.* 18, 1514).—2. From nitroso-*o*-cresol. 3. From sulpho-benzene-azo-*o*-cresol by reducing with Sn and HCl (Nölting a. Kohn, *B.* 17, 365).—White plates or needles; may be sublimed.—CrO_3 gives toluquinone. Salt.—B'HCl.

Amido-*o*-cresol $x=6$. [124°–128°]. From nitro-cresol [143°]. Stellate groups of needles (Ullmann, *B.* 17, 1962). Salt.—B'HCl.

Undetermined derivatives of amido-o-cresols.

Methyl ether $C_6H_3Me(OMe)(NH_2)$ [1:2:5?]. [53°] (Hofmann a. Miller, *B.* 14, 571).

Ethyl ether $C_6H_3Me(OEt)(NH_2)$ [1:2:x]. From ethyl nitro-*o*-cresol [71°] (Staedel a. Kayser, *A.* 217, 217; *B.* 15, 1134). Salts.—B'HCl 1½aq.—$B'_2H_2SO_4$.—$B'_2H_2PtCl_6$. *Acetyl derivative* $C_6H_3Me(OEt)(NHAc)$. [108°]. Trimetric plates (from water); tables (from ether); cubes (from benzene).

Amido-*m*-cresols $C_6H_3Me(OH)(NH_2)$ [1:3:x].

Amido-*m*-cresol $x=6$. [151°]. From sulpho-benzene-azo-*m*-cresol by reduction (Nölting a. Kohn, *B.* 17, 367). White warts. On oxidation with CrO_3 it gives toluquinone.

Undetermined derivative of an amido-m-cresol.

Ethyl ether $C_6H_3Me(OEt)(NH_2)$ [1:3:x]. An oil formed by reducing ethyl-nitro-*m*-cresol [54°] (Staedel, *A.* 217, 219). Salt.—$B'_2H_2C_2O_4$. *Acetyl derivative.* [114°]. Mass of needles (from water).

Amido-*p*-cresols $C_6H_3Me(OH)(NH_2)$ [1:4:x].

Amido-*p*-cresol $x=2$. [144°].

Formation. — 1. From nitro-*p*-cresol [78°] (Knecht, *A.* 215, 91).—2. From nitro-toluidine $C_6H_3Me.(NH_2)(NO_2)$ [1:4:2] (Wallach, *B.* 15, 2833).

Properties.—Colourless plates by sublimation.

Acetyl derivatives

$C_6H_3Me(OH)(NHAc)$ [178°]; sol. KOHAq.—$C_6H_3Me(OAc)(NHAc)$ [129°] (Maassen, *B.* 17, 608).

Methyl ether $C_6H_3Me(OMe)(NH_2)$. [47°]. From the nitro-compound (K.); needles, volatile with steam.

Amido-*p*-cresol $x=3$. [135°].

Formation. — 1. From nitro-*p*-cresol [33°] (Wagner, *B.* 7, 1270; Hofmann a. Miller, *B.* 14, 572).—2. By reducing benzene-azo-*p*-cresol or sulpho-benzene-azo-*p*-cresol (Nölting a. Kohn, *B.* 17, 360).

Properties.—White plates or needles; gives a red colour with Fe_2Cl_6. Salt.—B'HCl.

Reactions.—1. Gives a methenyl derivative when heated with formic acid (H. a. M.).—2. Gives, when heated with Ac_2O and NaOAc, an ethenyl derivative which is converted by boiling dilute H_2SO_4 into an acetyl derivative.

Acetyl derivative [160°]. Long needles.

Methyl ether $C_6H_3Me(OMe)(NH_2)$ [38°].

Ethyl ether $C_6H_3Me(OEt)(NH_2)$. [41°]. From the nitro-compound (Staedel a. Kayser, *B.* 15, 1134). Needles (from water) or plates (from other solvents). Salts.—B'HCl 1½aq.—$B'_2H_2SO_4$ 2aq. *Acetyl derivative* [107°].

Di-amido-*p*-cresol.

Ethyl ether $C_6H_2Me(OEt)(NH_2)_2$ [1:4:3:5]. From the nitro-compound (Staedel a. Kayser, *A.* 217, 221). Pleasant-smelling oil—B'HCl: silky needles.

Di-amido-cresol $C_6H_2Me(OH)(NH_2)_2$ [1:x:2:4]. From amido-toluene-azo-amido-cresol (Graeff, *A.* 229, 349); decomposes when liberated from its salts.—$B''H_2SO_4$aq; slender grey needles (from alcohol-ether).

AMIDO-CRESYL- *v.* AMIDO-TOLYL-.

AMIDO-CROTONIC ETHER. A name applied to the imide of aceto-acetic ether (*v.* p. 19).

AMIDO-CUMENE *v.* CUMIDINE.

Di-amido-cumene $C_9H_{14}N_2$ *i.e.* $Pr.C_6H_3(NH_2)_2$. [47°]. From the nitro-compound (Hofmann, *J.* 1862, 354).

Di-amido-pseudo-cumene $C_6HMe_3(NH_2)_2$ [1:3:4:5:6]. [92°]. *Formation.* -1. By reducing nitro-pseudo-cumidine [47°] (Edler, *B.* 18, 630). 2. By reducing amido-azo-cumene (Nölting a. Baumann, *B.* 18, 1147). *Properties.*—Needles or plates; gives with Fe_2Cl_6 a brownish-red colour and a quinone-like smell; also gives Ladenburg's aldehydine reaction.

AMIDO-ψ-CUMENOL $C_9H_{13}NO$ *i.e.* $C_6HMe_3(OH)(NH_2)$ [1:3:4:6:2] [167°]. *Amido-pseudo-cumenol; Oxy-cumidine.* Obtained by reducing benzene-azo-ψ-cumenol (Liebermann a. Kostanecki, *B.* 17, 886); or nitro-ψ-cumenyl nitrate (Auwers, *B.* 17, 2980). White needles (by sublimation); sol. KOHAq. Fe_2Cl_6 gives a red colouration. *Di-acetyl derivative* $C_6HMe_3(OAc)(NHAc)$, [186°]: needles.

AMIDO-CUMINIC ACID $C_{10}H_{13}NO_2$

***m*-Amido-cuminic acid** $Pr.C_6H_3(NH_2)CO_2H$ [1:2:4]. [129°]. *Amido-iso-propyl-benzoic acid.* Prepared by reducing *m*-nitro-cuminic acid [158°] (Paterno a. Fileti, *G.* 5, 383; Lippmann a. Lange, *B.* 13, 1661).—Tables; some of it occasionally crystallises from water in thin plates [104°] (Fileti, *G.* 10, 12). Fe_2Cl_6 give a violet-blue colouration with the hydrochloride. EtI at 100° gives a syrupy *ethyl-amido-cuminic acid.*

Salts.—AgA': white pp.—$ZnA'_2$3aq: needles. HA'HCl.—$(HA'HCl)_2PtCl_4$.—$(HA')_2H_2SO_4$.

Acetyl derivative. [248°-250°]. Slender needles, sl. sol. boiling alcohol, saponified by water at 230°.

Ethyl ether EtA'. Heavy oil.

Nitrile $Pr.C_6H_3(NH_2).CN$. [45°]. (305°). From nitro-cumino-nitrile.—Needles (from water) (Czumpelik, *B.* 2, 183). Salt.—$(B'HCl)_2PtCl_4$.

o-Amido-cuminic acid $Pr.C_6H_3(NH_2).CO_2H$. [1:3:4]. [115°]. Prepared by reducing *o*-nitro-cuminic acid with $FeSO_4$ and NH_3 (Widman, *B.* 19, 270).—Plates or tables.

Acetyl derivative $C_{10}H_{12}AcNO_2$. [246°]. Slender needles, sl. sol. alcohol, and ether; may be sublimed (Widman, *B.* 16, 2579).

Di-amido-cuminic acid $C_{10}H_{14}N_2O_2$ *i.e.* $Pr.C_6H_2(NH_2)_2CO_2H$. [192°]. Formed by reducing di-nitro-cuminic acid (Boullet, *C. R.* 43, 399; Lippmann, *B.* 15, 2144).—Yellowish plates, sol. hot water, alcohol, ether, alkalis and acids. Crystallises from water with aq.

Salts.—AgA'aq.—HA'HCl aq: large prisms.

AMIDO-CUMYL-ACRYLIC ACIDS $C_{12}H_{15}NO_2$

I. $Pr.C_6H_3(NH_2).CH:CH.CO_2H$ [1:3:4]. [165°]. From the nitro-acid, $FeSO_4$, and NH_3 (Widman, *B.* 19, 262).—Flat yellow prisms (from alcohol). Salt.—HA'HCl3aq: very slender needles, v. sl. sol. water; converted by boiling water into cumostyril or (B. 3)-iso-propyl-(Py. 3)-oxy-quinoline [169°]. *Acetyl derivative* $PrC_6H_3(NHAc).CH:CH.CO_2H$, [220°]: very thin needles (from alcohol).

II. $PrC_6H_3(NH_2).CH:CH.CO_2H$ [1:2:4]. [165°]. From the nitro-acid (Widman, *B.* 19, 415). Six-sided tables (from ether). Warm H_2SO_4 gives a magenta colour. Salts.—HA'HCl: flat needles. —$(HA'HCl)_2PtCl_4$2aq.—$(HA')_2H_2SO_4$5aq. *Acetyl derivatives* $C_{12}H_{14}AcNO_2$, [240°]: needles (from alcohol).—$C_{12}H_{13}Ac_2NO_2$. [236°].

AMIDO-ψ-CUMYLENE-ACETAMIDINE

$C_{11}H_{15}N_3$ *i.e.* $C_6Me_3(NH_2)<\genfrac{}{}{0pt}{}{N}{NH}>CMe$ [1:3:4:2:5/6].

Ethenyl-tri-amido-tri-methyl-benzene. [215°-218°]. From acetyl-di-nitro-pseudo-cumidine by reduction with Sn and HCl (Auwers, *B.* 18, 2663).—Rosettes of plates or yellowish prisms (from water) containing 2aq.

Salts.—B''2HClaq.—B''HCl 2aq.—$B''H_2PtCl_6$ aq.

AMIDO-CUMYL PHENYL KETONE *v.* PHENYL AMIDO-CUMYL KETONE.

***m*-AMIDO-CUMYL-PROPIONIC ACID** $C_{12}H_{17}NO_2$ *i.e.* $PrC_6H_3(NH_2).CH_2.CH_2.CO_2H$ [1:3]. [103°-105°]. From *m*-amido-cumyl-acrylic acid, NaOHAq, and sodium-amalgam (Widman, *B.* 19, 418). *Acetyl derivative* $C_{12}H_{16}AcNO_2$, [168°]; prisms (from alcohol).

AMIDO-DI-CYANIC ACID $C_2H_3N_3O$ *i.e.* $NH_2.CO.NH.CN$ or $HN:C<\genfrac{}{}{0pt}{}{NH}{NH}>CO$. *Allophano-nitrile; carbonyl guanidine; carbimido-cyanamide.*

Formation.—1. From di-cyano-di-amide and baryta-water.—2. From potassic cyanate and cold aqueous cyanamide (Hallwachs, *A.* 153, 239; Wunderlich, *B.* 19, 448).

Properties.—Plates. It decomposes carbonates and behaves as a strong acid. Produces biuret when warmed with H_2SO_4 (1 vol.) and water (2 vols.) at 70° (Baumann, *B.* 8, 708).

Salts.—$NaC_2H_2N_3O$.—KA'.—BaA'_2 3aq.—CuA'_2 4aq.—CuC_2HN_3O 2aq.—AgA'.

AMIDO-CYANURIC ACID *v.* AMMELIDE.

Di-amido-cyanuric acid *v.* AMMELINE.

AMIDO-CYMENE *v.* CYMIDINE.

Diamido-cymene $C_6H_2MePr(NH_2)_2$[1:4:3:6]. *Hydrochloride.* Formed by reducing the di-oxim of thymoquinone (Liebermann a. Ilinski, *B.* 18, 3200).

AMIDO-DRACYLIC ACID = *p*-AMIDO-BENZOIC ACID.

DI-AMIDO-DURYLIC ACID *v.* DI-AMIDO-TRI-METHYL-BENZOIC ACID.

AMIDO-ETHANE *v.* ETHYLAMINE.

Di-amido-ethane *v.* ETHYLENE DI-AMINE.

AMIDO-DI-ETHYL-ACETIC ACID *v.* AMIDO-HEXOIC ACID.

AMIDO-ETHYL ALCOHOL *v.* OXYETHYL-AMINE.

AMIDO-ETHYL-BENZENE *v.* AMIDO-PHENYL-ETHANE.

AMIDO-ETHYL METHYL KETONE *v.* METHYL AMIDO-ETHYL KETONE.

DI-AMIDO-DI-ETHYL OXIDE $C_4H_{12}N_2O$ *i.e.* $(CH_3.C(NH_2)H)_2O$.

Di-amido-ether. The very unstable hydrochloride (B'2HCl) of this body is formed by passing NH_3 into an ethereal solution of $(CH_3.CHCl)_2O$ (Hanriot, *A. Ch.* [5] 25, 224).

DI-AMIDO-DI-ETHYL-DIPHENYL $C_{16}H_{20}N_2$ *i.e.* [4:3:1] $NH_2.C_6H_3Et.C_6H_3Et.NH_2$ [1:3:4] (?). Formed by the action of $SnCl_2$ and HCl or H_2SO_4 on an alcoholic solution of *o*-azo-ethyl-benzene. —$B''H_2SO_4$: needles, sl. sol. water, m. sol. alcohol.

Acetyl derivative $C_{16}H_{16}(NHAc)_2$. [307°]. White needles (by sublimation), sl. sol. alcohol, sol. HOAc.

An isomeric di-amido-di-ethyl-diphenyl is formed similarly from *p*-azo-ethyl-benzene. Its sulphate is a white amorphous powder (G. Schultz, *B.* 17, 474).

AMIDO-ETHYL-TOLUENE *v.* AMIDO-TOLYL-ETHANE.

AMIDO-ETHYL-TOLUIDINE *v.* ETHYL-TOLYLENE DIAMINE.

AMIDO-ETHYL-*m*-URAMIDO-BENZOIC ACID $C_{10}H_{13}N_3O_3$ *i.e.* $NH_2.C_2H_4.NH.CO.NH.C_6H_4.CO_2H$. Formed by the action of ethylene diamine upon cyano-carboxamido-benzoic acid (*v.* AMIDO BENZOIC ACID). White prisms, sl. sol. cold water. Salt.—HA'HCl 2½aq (Griess, *B.* 18, 2416).

AMIDO-FLAVOLINE *v.* FLAVANILINE.

AMIDO-FLUORENE *v.* FLUORENE.

AMIDO-FORMIC ACID *v.* CARBAMIC ACID.

AMIDO-FURFUR-BUTYLENE OXIDE

$C_8H_{11}NO_2$ *i.e.* $C_4H_3O.C(NH_2)<\genfrac{}{}{0pt}{}{CMe_2}{O}$

(215°-220°). Obtained by reducing $C_8H_{10}N_2O_4$, the product of addition of N_2O_3 to furfur-butylene.

Properties.—Colourless liquid, volatile with steam, sol. water.

Salts.—B'HCl aq: crystals, v. sol. water.—$B'_2H_2PtCl_6$: sol. hot. water.

Acetyl derivative $C_8H_9O_2.NHAc$ [153°]; (305°-310°): needles, v. sol. HClAq.

Anhydride $C_8H_9NO.Ac$ [142°]. (300°-310°). V.D. 4·77. Formed from amido-furfur-butylene oxide on distilling, or even on keeping. It forms large colourless crystals, and is volatile with steam. It is a tertiary base (Tönnies a. Staub, *B.* 17, 854).

AMIDOGEN. The group NH_2; *v.* AMIDES, AMIDO-ACIDS, and AMINES.

AMIDO-GLUTARIC ACID *v.* GLUTAMIC ACID.

AMIDO-GLYCOLLIC ACID *v.* OXY-AMIDO-ACETIC-ACID.

AMIDO-HEMIPIC ACID *v.* HEMIPIC ACID.

AMIDO-HEPTOIC ACID $C_7H_{15}NO_2$ *i.e.* $C_5H_{11}.CH(NH_2).CO_2H$. *a-Amido-œnanthic acid.* From bromo-heptoic acid and alcoholic NH_3 at 100° (Helms, *B.* 8, 1168). Six-sided tables or plates, v. sl. sol. cold water, insol. alcohol.

Salts.—CuA'_2: insoluble powder.—HA'HCl: prisms, v. sol. water or alcohol.

AMIDO-HEXOIC ACID $C_6H_{13}NO_2$.

a-Amido-*n*-hexoic acid *v.* LEUCINE.

Amido-di-ethyl-acetic acid $CEt_2(NH_2).CO_2H$.

Preparation.—Di-ethyl ketone cyanhydrin, $CEt_2(OH).CN$, obtained by the action of dilute HCN on di-ethyl ketone, is heated with alcoholic NH_3, and the product is saponified by HCl.

Properties.—Thick tables or prisms (from water), v. sol. water, m. sol. alcohol, insol. ether; may be sublimed.

Salts.—AgA': white plates.—CuA'_2: violet plates.—HA'HCl: thick white prisms (Tiemann a. Friedländer, *B.* 14, 1975).

a-Amido-iso-butyl-acetic acid $Pr.CH_2.CH(NH_2).CO_2H$. S. ·85 at 12°. From iso-valeric aldehyde-ammonia, HCN and HClAq (Limpricht, *A.* 94, 243; Hüfner, *J. pr.* [2] 1, 10).

Properties.—Resembles leucine, but is optically inactive (Mauthner, *H.* 7, 223).

AMIDO-HEXYL ALCOHOL *v.* DI-ACETONE-ALCAMINE.

AMIDO-HIPPURIC ACID $C_9H_{10}N_2O_3$ *i.e.* $C_6H_4(NH_2).CO.NH.CH_2.CO_2H$.

m-Amido-benzoyl-glycocoll. [194°] (Conrad, *J. pr.* [2] 15, 258). S. ·3 at 20°; S. (alcohol) ·08 at 15°. From *m*-nitro-hippuric acid, ammonium sulphide and H_2S (Schwanert, *A.* 112, 70).

Properties.—Plates or needles. Soluble in alkalis and in acids. Salt.—B'HCl.

Reactions.—1. Boiling HCl forms *m*-amido-benzoic acid and glycocoll.—2. *Urea* forms uramido-hippuric acid $C_{10}H_{11}N_3O_4$ and a small quantity of carboxamido-hippuric acid $C_{19}H_{18}N_4O_7$ (Griess, *J. pr.* [2] 1, 135).

DI-AMIDO-HYDRO-ACRIDINE KETONE, so called, $C_{13}H_{11}N_3O$. [223°]. Formed by reducing the *o*-carboxylic acid of di-nitro-di-phenyl-amine with Sn and HCl. Flat needles or thick prisms, v. sol. hot alcohol, v. sl. sol. ether, benzene, cold water, and light petroleum. Fe_2Cl_6 gives a deep yellow colour, passing into greenish-black; $K_2Cr_2O_7$ gives a red pp.

Salt.—B'HCl: thin colourless needles, sl. sol. cold water.

Chloro-derivative $C_{13}H_{10}ClN_3O$. [c. 280°]. Formed by reducing chloro-di-nitro-di-phenyl-amine *o*-carboxylic acid. Colourless crystals, sol. hot water, v. sl. sol. cold water, ether, and benzene (Jourdan, *B.* 18, 1450).

AMIDO-HYDRATROPIC ACID *v.* AMIDO-PHENYL-PROPIONIC ACID.

DI-AMIDO-HYDRAZO-BENZENE *v.* HYDRAZINES.

AMIDO-HYDRO-CARBOSTYRIL $C_9H_{10}N_2O$.

Oxy-amido-di-hydro-quinoline.

(*B.* 3)-amido-hydro-carbostyril

$$C_6H_3(NH_2)\left<\begin{array}{l}CH_2.CH_2\\ \quad\;\;|\\ NH.CO\end{array}\right. \left[3:\begin{smallmatrix}6\\5\end{smallmatrix}\right]$$

Di-amido-phenyl-propionic anhydride. Di-amido-hydro-cinnamic anhydride. [211°]. Prepared by reducing di-nitro-phenyl-propionic acid with tin and HCl. It forms colourless needles or prisms, v. sol. hot water, alcohol, and HOAc, insol. CS_2.

Salts.—B'HCl: needles.—$B'_2H_2PtCl_6$: yellow leaflets. *Bromine* forms a mono-bromo-derivative, [210°] and a di-bromo-derivative, [179°], both crystallising in needles (Gabriel a. Zimmermann, *B.* 12, 601).

(*Py.* 4)-Amido-hydro-carbostyril

$$C_6H_4\left<\begin{array}{l}CH_2 - CH_2\\ \qquad\quad |\\ N(NH_2).CO\end{array}\right. . \quad [143°].$$

From $C_6H_4(NH.NH.SO_3Na)CH_2.CH_2.CO_2H$ (*v.* HYDRAZIDO-PHENYL-PROPIONIC ACID) by addition of HCl (Fischer a. Kuzel, *A.* 221, 282). Crystallised from water. Sol. water, v. sl. sol. alcohol. Does not reduce boiling Fehling's solution, but reduces hot Ag_2O. Salt.—$C_9H_{10}N_2OHCl$.

Reactions.—1. An acid solution is converted by $NaNO_2$ into hydro-carbostyril.—2. With EtI and alcohol at 100° it gives an ethyl derivative $C_6H_4\left<\begin{array}{l}CH_2 - CH_2\\ N(NHEt).CO\end{array}\right>$. [74°]. This gives a nitrosamine with $NaNO_2$ and HCl.

AMIDO-HYDRO-CINNAMIC ACID *v.* AMIDO-PHENYL-PROPIONIC ACID.

DI-AMIDO-DI-HYDRO-TERE-PHTHALIC ACID

$$\begin{array}{l}NH_2.C.CH(CO_2H).CH\\ \quad\;\;\|\qquad\qquad\qquad\;\|\\ H.C.CH(CO_2H).C.NH_2\end{array}$$

(?) *Di-imido-hexa-hydro-terephthalic acid or succino-succinic-acid-di-imide.*

Ethyl ether $A''Et_2$ [181°]. Obtained by fusing di-oxy-di-hydro-terephthalic ether (succino-succinic ether) with ammonium acetate. Yellow needles; sl. sol. alcohol and ether with a green fluorescence, v. sol. chloroform. By treatment with bromine in H_2SO_4 solution it is converted into di-amido-terephthalic ether. The hydrochloride and sulphate are colourless sparingly soluble salts (Baeyer, *B.* 19, 429).

AMIDO-TETRA-HYDRO-QUINOLINE

$$C_9H_{12}N_2 \textit{ i.e. } C_6H_4\left<\begin{array}{l}CH_2 - CH_2\\ \qquad\quad |\\ N(NH_2).CH_2.\end{array}\right.$$

[56°]. (c. 255°). Prepared by reducing the nitrosamine of tetra-hydro-quinoline with zinc dust and HOAc. White crystals.

Salts.—$B'_2H_2SO_4$ 2aq: yellow plates, sl. sol. cold water.—The hydrochloride is v. sol. water.

Reactions.—Reduces salts of Au and Pt, and Fehling's solution. Ppd. HgO forms an azo-quinoline (Hoffmann a. Königs, *B.* 16, 780).

AMIDO HYDRO-QUINONE $C_6H_7NO_2$ *i.e.* $NH_2.C_6H_3(OH)_2$.

Di-methyl derivative $NH_2.C_6H_3(OMe)_2$. [82°]. (270°). Formed by reducing the di-methyl-derivative of nitro-hydroquinone. Pearly plates, sol. hot water, alcohol, benzene, light petroleum and CS_2. Very readily oxidised.

Reactions.—1. $CuSO_4Aq$ gives a greenish-black colour.—Fe_2Cl_6 pps. lustrous greenish plates, which form a red solution in water.—$AgNO_3$ gives a silver mirror. Salts.—$^xB'HCl$: white needles.—$^xB'_2H_2PtCl_6$: brown pp.

Acetyl derivative.—$C_6H_3(NHAc)(OMe)_2$. [91°]. Silvery scales; sol. water, alcohol, benzene, light petroleum and CS_2 (Magatti, *B.* 14, 70; *G.* 1881, 352; Mülhäuser, *A.* 207, 254; Baessler, *B.* 17, 2119).

Ethyl derivative $C_6H_3(NH_2)(OEt)(OH)$. From the nitro-compound (Weselsky a. Benedikt, *M.* 2, 370).—B'HCl.

Di-amido-hydroquinone $C_6H_2(OH)_2(NH_2)_2$. Formed by reduction of di-nitro-hydroquinone or its di-acetyl derivative with tin and HCl. Owing to its easy oxidisability the base was not isolated in the free state. $B''H_2Cl_2$.—Colourless needles, v. e. sol. water, sl. sol. conc. HCl.

Di-acetyl derivative $C_6H_2(OH)_2(NHAc)_2$. [c. 240°]. Colourless needles. Is oxidised to di-acetyl-di-amido-quinone $C_6H_2O_2(NHAc)_2$.

Tetra-acetyl derivative $C_6H_2(OAc)_2(NHAc)_2$. [216°]; colourless needles or plates; v. sol. alcohol and acetic acid, sl. sol. water and ether. Dissolves in dilute alkalis, the solution becomes oxidised on exposure to the air and deposits yellow needles of the above-mentioned di-acetyl-di-amido-quinone (Nietzki a. Preusser, *B.* 19, 2247).

Di-methyl-derivative $C_6H_2(NH_2)_2(OMe)_2$. The hydrochloride of this body is formed by reducing the corresponding nitro compound. It crystallises in needles, [169°] (Kariof, *B.* 13, 1676).

Di-methyl-di-amido-hydroquinone (*q. v.*) is isomeric with this body.

DI-AMIDO-DI-IMIDO-BENZENE

$C_6H_2(NH_2)_2(NH)_2$ [1:2:4:5]. Small brown needles. Formed by oxidation of solutions of salts of tetra-amido-benzene with Fe_2Cl_6, &c.

Salts.—$B''H_2Cl_2$: glittering brown needles, sparingly soluble in water with a bluish-violet colour.—$B''(HNO_3)_2$: small green needles (Nietzki a. Hagenbach, *B.* 20, 335).

AMIDO-IMIDO-METHANE *v.* FORMAMIDINE.

AMIDO-DI-IMIDO-(α)-NAPHTHOL

$C_{10}H_9N_3O$ *i.e.* $C_{10}H_4(NH_2)(OH)\langle{NH \atop NH}$ (?). Prepared by the reduction of tri-nitro-(α)-naphthol with tin and HCl. Brown scales, insol. water and ether. Salts.—B'HCl: lustrous green scales, sl. sol. cold water.—$B'_2H_2PtCl_6$ (Diehl a. Merz, *B.* 11, 1663).

AMIDO-DI-IMIDO-ORCIN $C_7H_9N_3O_2$ 2aq *i.e.* $C_6Me(NH_2)(OH)_2\langle{NH \atop NH}$ (?). Prepared by reducing tri-nitro-orcin with sodium-amalgam (Stenhouse, *A.* 167, 167). Lustrous green needles, v. sl. sol. water, insol. alcohol, ether, and benzene. NaOHAq forms a deep blue solution. Reduced by further action of sodium-amalgam to tri-amido-orcin. Salts.—B'HCl aq: brownish-red needles; sol. water but ppd. by HCl.—$B'_2H_2SO_4$ 2aq: purple laminæ.

AMIDO-DI-IMIDO-PHENOL, so called.

$C_6H_7N_3O$ *i.e.* $C_6H_2(NH_2)_2\langle{NH \atop O}$ $\left[2:6:{1 \atop 4}\right]$.

Di-amido-quinone-imide (Hepp, *A.* 215, 351). The hydrochloride, B'HCl, separates as brown needles with [illegible] when Fe_2Cl_6 is added to a conc. aqueous solution of the hydrochloride of tri-amido-phenol (Heintzel, *Z.* 1867, 342). It is decomposed by alkalis and by hot water; hot dilute HCl changes it into colourless needles of the hydrochloride of oxy-amido-quinone-imide (or di-amido-quinone) $C_6H_6N_2O_2HCl$, while H_2SO_4 forms a corresponding sulphate crystallising in plates.

AMIDO-IMIDO-DI-PHENYL SULPHIDE

$C_{12}H_{10}N_2S$ *i.e.* $HN\langle{C_6H_4 \atop C_6H_3(NH_2)}\rangle S$. *Amido-thio-di-phenyl-imide; Amido-sulphido-di-phenyl-imide.*

Formation.—1. By reduction of nitro-imido-di-phenyl-sulphoxide, $HN\langle{C_6H_4 \atop C_6H_3(NH_2)}\rangle SO$.—2. By heating *p*-amido-di-phenyl-amine with sulphur (Bernthsen, *B.* 17, 2858; *A.* 230, 101). White satiny plates (from water); m. sol. hot water, v. sol. alcohol and ether. Turns grey in moist air. Fe_2Cl_6 converts it into the following body:

Imido-imido-di-phenyl sulphide $C_{12}H_8N_2S$ *i.e.* $N\langle{C_6H_4 \atop C_6H_3}\rangle S$, with NH linked to N and C_6H_3. Small brown crystals, v. sol. alcohol, sl. sol. water and ether. Its salts dye silk greyish-violet. It is easily reduced to the preceding body. Salts.—B'HCl ½aq.—$B'_2H_2ZnCl_4$: brown needles or prisms.

Di-amido-imido-di-phenyl sulphide

$C_{12}H_{11}N_3S$ *i.e.* $HN\langle{C_6H_3(NH_2) \atop C_6H_3(NH_2)}\rangle S$. Formed by reducing (α)-di-nitro-imido-di-phenyl sulphoxide with tin and HCl, or Lauth's violet with ammonium sulphide (Bernthsen, *B.* 17, 614). Yellow needles or plates; sl. sol. water and ether. The sulphate is sl. sol. water.

Amido-imido-imido-di-phenyl-sulphide

$C_{12}H_9N_3S$ *i.e.* $N\langle{C_6H_3(NH_2) \atop C_6H_3}\rangle S$, with NH linked to N and C_6H_3. *Lauth's Violet.*

Formation.—1. By treating a solution of *p*-phenylene diamine hydrochloride with H_2S and Fe_2Cl_6 successively (Lauth, *C. R.* 82, 1441; Koch, *B.* 12, 592, 2069).—2. By action of Fe_2Cl_6 on the preceding body (B.). Its alcoholic solution has a violet colour with reddish-brown fluorescence. Its solution in excess of HCl is blue; in H_2SO_4, green changing to blue and then to violet. Long heating with MeI converts it into the methylo-iodide of penta-methyl-di-amido-imido-di-phenyl sulphide identical with that formed in the same way from methylene blue. Salt.—B'HCl: green crystals, sl. sol. cold water.

An isomeride (*Bernthsen's Violet*) is formed by reducing (β)-di-nitro-imido-di-phenyl sulphoxide and then oxidising the leuco-base with Fe_2Cl_6. Its hydrochloride B'2HCl, forms dark

needles, which dye reddish-violet. H_2SO_4 forms a violet solution.

AMIDO-DI-IMIDO RESORCIN $C_6H_7N_3O_2$ aq or $C_6H(OH)_2(NH_2)<\overset{NH}{\underset{NH}{|}}$ (?). From tri-amido-resorcin hydrochloride and Fe_2Cl_6. Lustrous green needles, v. sl. sol. water, insol. alcohol or ether: KOHAq forms a blue solution. Dilute HCl at 170° forms tri-oxy-quinone.

Salt.—B'HCl: red needles, ppd. by HCl (Schreder, *A.* 158, 250; Diehl a. Merz, *B.* 11, 1229).

AMIDO-INDIGO $C_{16}H_{12}N_4O_2$ *i.e.* $C_{16}H_8(NH_2)_2N_2O_2$. Prepared by reducing nitro-indigo with acetic acid and powdered zinc (Baeyer, *B.* 12, 1317). Dark violet pp., v. sl. sol. alcohol, ether and chloroform. Forms blue solutions in dilute acids.

AMIDO-ISATIN, so called, *v.* ISATINIMIDE.

AMIDO-LACTIC ACID *v.* OXY-AMIDO-PROPIONIC ACID.

AMIDO-MALEÏC ACID $C_4H_5NO_4$ *i.e.* $CO_2H.CH:C(NH_2).CO_2H$. [182°]. Easily soluble crystals. Prepared by saponification of the amides.—$A''Ag_2$: voluminous pp., explosive.

Di-ethyl ether Et_2A''. [100°]. Colourless prisms. Sol. alcohol and ether, insol. water. Prepared by the action of alcoholic NH_3 (2 mols.) on chloro-maleïc ether (1 mol.).

Amido-maleamic-ethyl ether $C_2H(NH_2)<\begin{smallmatrix}CO.NH_2\\CO_2Et\end{smallmatrix}$. [62°]. Long white prisms. V. sol. alcohol and ether, insol. cold water. Prepared by the action of alcoholic NH_3 (3 mols.) on chloro-maleic ether (1 mol.).

Diamide $C_2H(NH_2)<\begin{smallmatrix}CO.NH_2\\CO.NH_2\end{smallmatrix}$. [122°]. Colourless plates. Sol. alcohol, ether, and hot water. Prepared by the action of an excess of strong alcoholic NH_3 on chloro-maleïc ether (Claus a. Voeller, *B.* 14, 150).

AMIDO-MALONIC ACID $C_3H_5NO_4$ *i.e.* $CH(NH_2)(CO_2H)_2$. Obtained from nitroso-malonic acid by reducing with sodium-amalgam (Baeyer, *A.* 131, 295). Prisms (from water) or needles (by ppg. with alcohol). When heated alone, or in aqueous solution, it splits up into CO_2 and glycocoll. Iodine oxidises it, in aqueous solution, forming mesoxalic acid.

Salt.—$Pb(C_3H_4NO_4)_2$: crystalline pp.

Amide $CH(NH_2)(CO.NH_2)_2$. [182°]. Formed by heating chloro-malonic ether with alcoholic NH_3. Prisms, sol. hot water (Conrad a. Guthzeit, *B.* 15, 607).

AMIDO-MESITOL $C_9H_{13}NO$ *i.e.* $C_6HMe_3(NH_2)(OH)$ [1:3:5:2:4]. A very oxidisable body formed by reduction of nitro-mesitol.—B'HCl: needles (Knecht, *B.* 15, 1376).

AMIDO-MESITYLENE *v.* MESIDINE.

Di-amido-mesitylene $C_9H_{14}N_2$ *i.e.* $C_6HMe_3(NH_2)_2$. [90°]. From di- or tri-nitro-mesitylene with tin and HCl. Long slender needles (from water), or large monoclinic crystals (from ether). Sublimes in needles. V. sol. alcohol or ether, m. sol. hot water. CrO_3 oxidises it to oxy-iso-xyloquinone, $C_6HMe_2(OH)O_2$.

Salts.—B''2HCl: square tables (from water), ppd. by HCl.—$B''H_2C_2O_4$: hard grains (from water).—$B''H_2SO_4$: broad laminæ (from water).

Di-acetyl derivative, [above 360°]; v. sl. sol. water or cold alcohol (Fittig, *A.* 141, 134; 180, 27; Ladenburg, *A.* 179, 176).

AMIDO-MESITYLENIC ACID $C_9H_{11}NO_2$.

o-Amido-mesitylenic acid $C_6H_2Me_2(NH_2).CO_2H$ [1:3:4:5]. [187°] (Schmitz, *A.* 193, 171). [190°] (Jacobsen, *B.* 11, 2055). From the nitro acid with tin and HCl. Long needles (from alcohol). Splits up when heated with lime into CO_2 and (1, 3, 4)-xylidine.

p-Amido-mesitylenic acid $C_6H_2Me_2(NH_2)CO_2H$ [1:3:2:5]. [235°]. From the nitro acid. Long needles (from alcohol). Sl. sol. water, v. sol. hot alcohol. Gives (1, 3, 2)-xylidine when heated with lime.

Salt.—B'HCl: long needles (Fittig a. Brückner, *A.* 147, 50; Jacobsen, *B.* 12, 608).

AMIDO - METHENYL - AMIDO - PHENYL MERCAPTAN $C_7H_6N_2S$ *i.e.* $C_6H_4<\begin{smallmatrix}N\\S\end{smallmatrix}>C.NH_2$. [129°]. Prepared by heating chloro-methenyl-amido-phenyl mercaptan with alcoholic NH_3 at 160°. Nacreous laminæ. Fusion with potash produces amido-phenyl mercaptan.

Salt.—It is a weak base, and has a crystalline platinochloride, $B'_2H_2PtCl_6$ (Hofmann, *B.* 12, 1129; 13, 11).

AMIDO-METHOXY COMPOUNDS *v.* Methyl derivatives of OXY-AMIDO COMPOUNDS.

AMIDO-DI-METHYL-ACETIC ACID *v.* AMIDO-*iso*-BUTYRIC ACID.

DI-AMIDO-TETRA-METHYL-DI-AMIDO-DIPHENYL *v. Tetra* - METHYL - *tetra* - AMIDO-DIPHENYL. And, in general, amido-methyl-amido compounds are described as methyl-(di)-amido compounds.

AMIDO - DI - METHYL - ANILINE *v. Di*-METHYL-PHENYLENE DIAMINE.

AMIDO - METHYL - ANTHRACENE DIHYDRIDE $C_{15}H_{15}N$ *i.e.* $C_{14}H_{10}Me.NH_2$. [79°]. Prepared by heating amido-methyl-anthraquinone with HI and P at 150°. Glistening laminæ, which begin to sublime at 130° and are sol. alcohol, ether, chloroform, benzene, glacial acetic acid, and CS_2, but v. sl. sol. water.

Reactions.—1. *Nitrous acid* gives a green colour, and on adding NH_3, a red pp.—2. *Arsenic acid* gives a brownish-red mass after fusion. Salt.—B'HCl [245°]: glistening needles.

Acetyl derivative $C_{15}H_{14}AcN$. [198°]. White needles, sol. alcohol and ether (Roemer, *B.* 16, 1631).

AMIDO-METHYL-ANTHRANOL $C_{15}H_{13}NO$ *i.e.* $C_{12}H_6Me(NH_2)<\overset{C.OH}{\underset{CH}{|}}$. [183°]. Prepared by heating amido-methyl-anthraquinone with HI (S.G. 1·96) and P. Crystallises in nearly white needles, but sublimes in red needles. Sol. alcohol, ether, benzene, and glacial acetic acid, v. sl. sol. water.

Reactions.—1. H_2SO_4 gives a yellow solution, becoming purple-red on warming. — 2. HNO_3 gives a violet colour, turning red.—3. *Air* reconverts it, in alkaline solution, into amido-methyl-anthraquinone.

Di-acetyl derivative $C_{15}H_{11}Ac_2NO$. [170°]. Thick white needles; its alcoholic solution exhibits blue fluorescence (Roemer a. Link, 16, 703).

AMIDO-METHYL-ANTHRAQUINONE $C_{15}H_{11}NO_2$ *i.e.* $C_{14}H_6O_2(CH_3)(NH_2)$. [202°]. Prepared by reduction of nitro-methyl-anthraqui-

none. Long dark red needles. V. sol. alcohol, ether, benzene, acetic acid, and chloroform, v. sl. sol. water.

Acetyl derivative $C_{14}H_8O_2(CH_3)NHAc$. [177°]. Small light-red needles, sol. alcohol and glacial acetic acid (Römer a. Link, *B.* 16, 698).

AMIDO-METHYL BENZENE *v.* TOLUIDINE and BENZYLAMINE.

Amido-di-methyl-benzene *v.* XYLIDINE.

Amido-tri-methyl-benzene *v.* MESIDINE and ψ-CUMIDINE.

Amido-tetra-methyl-benzene *v.* DURIDINE.

Amido - penta - methyl - benzene *v.* *Penta*-METHYL-PHENYL-AMINE.

DI-AMIDO-TETRA-METHYL-BENZIDINE *v.* *Tetra*-METHYL-*tetra*-AMIDO-*di*-PHENYL.

AMIDO-METHYL-BENZOIC ACID *v.* AMIDO-TOLUIC ACID.

Amido - di - methyl - benzoic acid *v.* AMIDO-MESITYLENIC ACID.

Di-amido-tri-methyl-benzoic acid $C_{10}H_{14}N_2O_2$ *i.e.* $C_6Me_3(NH_2)_2CO_2H$ [6:4:3:5:2:1]. *Di-amido-durylic acid.* [221°]. Formed by reducing the di-nitro compound with zinc dust and dilute HOAc. Colourless silky needles, sol. hot water and hot alcohol, v. sl. sol. ether. Fe_2Cl_6 oxidises it to pseudo-cumo-quinone carboxylic acid (Nef, *B.* 18, 3496; *A.* 237, 1).

Acetyl-derivative [275°].

AMIDO-TRI-METHYL-BUTYL-LACTIC ACID *v.* OXY-AMIDO-HEPTOIC ACID.

***m*-AMIDO-α-METHYL-CINNAMIC ALDEHYDE** $C_{10}H_{11}NO$ *i.e.* $C_6H_4(NH_2).CH:CMe.CHO$ [60°]. Got by reducing the nitro compound with $FeSO_4$ and NH_3. Yellowish crystals; dissolves in aqueous acids, and reduces ammoniacal $AgNO_3$.

Phenyl hydrazide $C_6H_4(NH_2).CH:CMe.CH:N_2HPh$; [157°]: needles.

Acetyl derivative $C_6H_4(NHAc).CH:CMe.CHO$; [120°]: short thick prisms (Miller a. Kinkerlin, *B.* 19, 1248).

AMIDO - (*B.* 2-*Py.* 2) - DI-METHYL - (*Py.* 3)-ETHYL-QUINOLINE $C_{13}H_{16}N_2$ *i.e.* $C_9H_3N(NH_2)Me_2Et$. [149°]. Plates, monoclinic tables, prisms or flat needles. Formed by reduction of the nitro-derivative with $SnCl_2$. Salts.—B'HCl; very soluble colourless crystals. The nitrate and sulphate are also easily soluble in water (Harz, *B.* 18, 3392).

AMIDO - (*Py.* 4)-METHYL-HYDRO-QUINOLINE

$$C_{10}H_{14}N_2 \text{ i.e. } C_6H_3(NH_2)\left\langle\begin{matrix}CH_2.CH_2\\ |\\ NMe.CH_2\end{matrix}\right.$$

Amido-kairoline. Yellowish oxidisable oil. Formed by reduction of nitro-kairoline [94°] with $SnCl_2$. By nitrous acid it is converted into a compound $C_{10}H_{13}N_3O$, [144°] when dry, which crystallises with 5aq in splendid red needles, and dissolves in dilute acids with a deep red colour.

Salts.—The acid tartrate forms sparingly soluble crystals. $B''H_2Cl_2PtCl_4$ (Feer a. Koenigs, *B.* 18, 2391).

AMIDO DI-METHYL-HYDROQUINONE *v.* *di-methyl*-AMIDO-HYDROQUINONE.

AMIDO-TRI-METHYL-PHENYL-ACETAMIDINE *v.* AMIDO-ψ-CUMYLENE-ACETAMIDINE.

AMIDO-DI-METHYL-PHENYL-ACETIC ANHYDRIDE *v.* *Di*-METHYL-OXINDOLE.

AMIDO-METHYL-PROPYL-BENZENE *v.* CYMIDINE.

(*B.* 4)-AMIDO-(*Py.* 3)-METHYL-QUINOLINE $C_{10}H_{10}N_2$ *i.e.* $C_9H_5(CH_3)(NH_2)N$. *o-Amido-quinaldine.* [56°]. Formed by reduction of (*B.* 4)-nitro-(*Py.* 3)-methyl-quinoline. Long prisms. V. sol. alcohol, ether, and hot ligroine, sparingly in water.—B'HCl: yellow needles (Doebner a. Miller, *B.* 17, 1701).

(*B.* 1 or 3)-Amido-(*Py.* 3)-methyl-quinoline $C_{10}H_{10}N_2aq$ *i.e.* $C_9H_5(CH_3)(NH_2)N$ *m-Amido-quinaldine* [105°] when [illegible]. Formed by reduction of (*B.* 1 or 3)-nitro-(*Py.* 3)-methyl-quinoline. Colourless crystals (+H_2O). V. sol. hot water, alcohol, and benzene, sparingly in ether. B'HCl: red needles (Doebner a. Miller, *B.* 17, 1702).

Amido-(*B.* 2, 4-*Py.* 3)-tri-methyl-quinoline $C_{12}H_{14}N(NH_2)$. Formed by reducing nitro-tri-methyl-quinoline with $SnCl_2$. Yellowish plates (from alcohol) (Panajotow, *B.* 20, 36).

Sulphonic acid $C_{12}H_{11}(SO_3H)(NH_2).N$. Small yellow needles. BaA'_2 3aq: silky needles, sl. sol. cold water.

AMIDO-METHYL-TOLUIDINE *v.* METHYL-TOLYLENE DIAMINE.

AMIDO-β-METHYL UMBELLIFERON

$$C_{10}H_9NO_3 \text{ i.e. } C_6H_2(NH_2)(OH)\left\langle\begin{matrix}CMe:CH\\ |\\ O\ .\ CO\end{matrix}\right. \quad [247°].$$

From nitro-β-methyl-umbelliferon. Needles, sparingly soluble in the usual menstrua. Fe_2Cl_6 gives an intense green colouration with the alcoholic solution.

Salt.—$B'_2H_2SO_4$ 2aq: sparingly soluble pp. (Pechmann a. Cohen, *B.* 17, 2137).

AMIDO-METHYL-URACIL *v.* URAMIDO-CROTONIC ACID.

AMIDO-NAPHTHALENE *v.* NAPHTHYLAMINE.

Di - amido - naphthalene *v.* NAPHTHYLENE DIAMINE.

Tri-amido-naphthalene $C_{10}H_{11}N_3$ *i.e.* $C_{10}H_5(NH_2)_3$. The *hydriodide*, B'''3HI, is formed from (β)-tri-nitro-naphthalene [218°], by reducing it (1 g.) with I (20 g.), P (4 g.) and water; it forms white needles; at 70° it becomes B'''2HI. The *sulphate*, $B'''H_2SO_4$ forms silky needles. The free base is very unstable.

Benzoyl derivative $C_{17}H_{15}N_3O$ *i.e.* $C_{10}H_5(NH_2)_2(NHBz)$[2:4':1]. From benzoyl-di-nitro-naphthylamine.

Salts. — B'''HCl: needles. — $B'''H_2SO_4$: needles (Lautemann a. Aguiar, *Bl.* [2] 3, 263; Hübner a. Ebell, *A.* 208, 324).

Tetra-amido-naphthalene $C_{10}H_{12}N_4$ *i.e.* $C_{10}H_4(NH_2)_4$. The hydriodide B''''4HI, formed by reducing (β)-tetra-nitro-naphthalene [200°] with P, I, and water, crystallises in yellowish laminæ, sol. water and alcohol (L. a. A.).

AMIDO-NAPHTHALENE SULPHONIC ACID *v.* NAPHTHYLAMINE SULPHONIC ACID.

AMIDO-(β)-NAPHTHO-HYDROQUINONE $C_{10}H_9NO_2$ *i.e.* $C_{10}H_5(NH_2)(OH)_2$. *Amido-di-oxy-naphthalene.* The *hydrochloride*, B'HCl, is got by reducing nitro-(β)-naphthohydroquinone with tin and HCl (Groves, *C. J.* 45, 300). It is rapidly oxidised by air.

AMIDO-NAPHTHOIC ACID $C_{11}H_9NO_2$ *i.e.* $C_{10}H_6(NH_2).CO_2H$.

Amido-(α)-naphthoic acid. [212°]. From nitro-(α)-naphthoic acid, [230°], by reducing with $FeSO_4$ and NH_3. Colourless needles; may be sublimed; sol. alcohol, v. sl. sol. ether (Ekstrand, *B.* 18, 78).

Amido-(β)-naphthoic acid. [211°]. Formed by reducing nitro-(β)-naphthoic acid [269°], with $FeSO_4$ and NH_3. Slender colourless needles (Ekstrand, *B.* 18, 1206).

Amido-(β)-naphthoic acid. [219°]. From nitro-(β)-naphthoic acid [289°]. Slender needles. Salts.—$^{*}HA'HCl$: small prisms, v. sol. water. — $^{*}HA'HNO_3$: large thin laminæ.— $^{*}(HA')_2H_2SO_4$: small prismatic needles (E.).

Amido-(β)-naphthoic acid. [232°]. From nitro-(β)-naphthoic acid [293°]. Small trimetric tables; sol. alcohol and boiling water. Salts.— CaA'_2 4aq: long violet needles. — $HA'HNO_3$: large needles.—$(HA')_2H_2SO_4$: needles (E.).

peri-**Amido-naphthoic acid** $C_{10}H_6(NH_2)CO_2H$ [a_1 a'_1].

Preparation.—The crude product of the nitration of (α)-naphthoic acid is reduced with $FeSO_4$. The solution is boiled with HCl and, on cooling, the lactam of the peri-acid, [178°], crystallises out in yellow needles, whilst the hydrochloride of the isomeric acid remains in solution.

By diazotisation, treatment with cuprous cyanide, and saponification of the nitrile, naphthalic acid is formed (Bamberger a. Philip, *B.* 20, 242). This experiment determines the constitution of acenaphthene (*q. v.*) which may be oxidised to naphthalic acid.

Lactam $C_{11}H_7NO$

i.e. $C_{10}H_6\langle{}^{CO}_{NH}\rangle$. [179°].

Formed by reducing nitro-(α)-naphthoic acid [215°]. Needles (by sublimation); sol. hot alcohol, sl. sol. water and ether. It is an indifferent substance insoluble in alkaline carbonates, but soluble in hot aqueous NaOH with formation of the acid (Ekstrand, *B.* 18, 75; 19, 1137; compare Rakowsky, *B.* 5, 1020).

Acetyl derivative $C_{11}H_6AcNO$. [125°]. Long hair-like needles (from alcohol).

AMIDO-NAPHTHOL $C_{10}H_9NO$.

(α)-Amido-(α)-naphthol $C_{10}H_6(OH)(NH_2)$ [1:4]. Formed by reducing nitro-(α)-naphthol [164°] (Liebermann, *A.* 183, 247) or *p*-sulpho-benzene-azo-(α)-naphthol (Liebermann, *B.* 14, 1796).

The free base is unstable; its salts produce (α)-naphthoquinone when oxidised.

B'HCl: white needles; converted by bleaching powder into $C_{20}H_{10}N_3Cl$ or $C_{20}H_{12}N_3Cl$ which separates from HOAcAq in needles [85°], and explodes at 130° (Hirsch, *B.* 13, 1910).

(β)-Amido-(α)-naphthol $C_{10}H_6(OH)(NH_2)$ [1:2]. Formed by reducing nitro-(α)-naphthol [128°], or nitroso-(α)-naphthol (L.).

The free base is unstable; in presence of alkalis, air forms violet naphthoquinone-imide, $C_{10}H_6\langle{}^{NH}_{O}$. Its salts give (β)-naphthoquinone when oxidised. B'HCl: white laminæ.— $B'C_6H_2(NO_2)_3OH$.

(α)-Amido-(β)-naphthol $C_{10}H_6(OH)(NH_2)$. Formed by reducing nitro-(β)-naphthol [103°] (Jacobsen, *B.* 14, 806; *A.* 211, 48) or nitroso-(β)-naphthol (Groves, *C. J.* 45, 296).

Preparation.—(β)-naphthol orange is heated with HClAq and $SnCl_2$ in slight excess over that required by the equation:

$$HO.C_{10}H_6.N_2.C_6H_4.SO_3Na + 2SnCl_2 + 6HCl = HO.C_{10}H_6.NH_2HCl + NH_2.C_6H_4.SO_3H + 2SnCl_4 + NaCl,$$

Amido-(β)-naphthol hydrochloride crystallises on cooling, and is freed from sulphanilic acid by washing with NaOHAq (Groves, *C. J.* 45, 291).

Properties.—Colourless scales, v. sl. sol. water, readily oxidised by air. Its ethereal solution fluoresces violet. *Chromic mixture* oxidises it to (β)-naphthoquinone.

Salt.—B'HCl: white needles.

Benzoyl derivative.—$C_{10}H_6(NHBz)OH$. [245°]. Small colourless plates, soluble in alkalis. Formed by reduction of the benzoyl-derivative of (α)-nitro-(β)-naphthol, the benzoyl group wandering from the hydroxyl to the amidogen; this probably takes place by the intermediate formation of benzenyl-amido-naphthol $C_{10}H_6\langle{}^{N}_{O}\rangle C.C_6H_5$ since this body occurs in the reduction product.

Acetyl derivative. — $C_{10}H_6(NHAc)OH$. [225°]. Plates. Formed by reduction of the acetyl derivative of (α)-nitro-(β)-naphthol, the same isomeric change taking place as in the preceding case (Böttcher, *B.* 16, 1935).

Di-amido-(α)-naphthol $C_{10}H_{10}N_2O$ *i.e.* $C_{10}H_5(OH)(NH_2)_2$. From di-nitro-(α)-naphthol [138°] (Griess a. Martius, *A.* 134, 376). Its aqueous solution is turned red by Fe_2Cl_6, amido-naphthoquinone imide (*q. v.*) being formed.

Salts. (Graebe a. Ludwig, *A.* 154, 307).— $B''H_2SnCl_4$: monoclinic prisms, $a:b:c$ = 1·184:1:1·487, $\beta = 72° 33'$. — $B''H_2SnCl_4$ 4aq.— $B''H_2SO_4$ 2aq.

Tri-amido-(α)-naphthol $C_{10}H_{11}N_3O$ *i.e.* $C_{10}H_4(OH)(NH_2)_3$. From tri-nitro-(α)-naphthol (Diehl a. Merz, *B.* 11, 1665; Ekstrand, *B.* 11, 161).

$B'''H_2SO_4$aq: scales.—$B'''3HCl$ aq: needles.

AMIDO-(β)-NAPHTHOL SULPHONIC ACID. $C_{10}H_5(OH)(NH_2).SO_3H$. From nitroso-(β)-naphthol sulphonic acid (*q. v.*) with tin and HCl (Meldola, *C. J.* 39, 47). Long white needles, v. sol. water, turned brown by air. Gives phthalic acid with HNO_3Aq. The acid obtained by reducing *m*-carboxy-benzene-azo-sulpho-(β)-naphthol appears to be an isomeride (Griess, *B.* 14, 2032).

Di-Amido-(α)-naphthol-sulphonic acid $C_{10}H_4(OH)(NH_2)_2SO_3H$ [1:2:4:β']. Prepared by reducing naphthol yellow S. Laminæ; gives di-imido-(α)-naphthol sulphonic acid when oxidised (Lauterbach, *B.* 14, 2029).

Amido-(β)-naphthol di-sulphonic acid $C_{10}H_4(OH)(NH_2)(SO_3H)_2$3aq. From *m*-carboxy-benzene-azo-sulpho-(β)-naphthol by reduction. Laminæ, v. sol. water (Griess, *B.* 14, 2042).

AMIDO-NAPHTHOQUINONE $C_{10}H_7NO_2$ *i.e.* $C_{10}H_5(NH_2)O_2$. *Oxy-naphtho-quinone imide. Oximido-naphthol.* Orange needles, formed by boiling amido-naphthoquinone imide with water (Martius a. Griess, *A.* 134, 377; Graebe a. Ludwig, *A.* 154, 307). Sl. sol. boiling water, v. sol. alcohol, insol. ether. Converted by boiling *acids* or *alkalis* into oxy-naphthoquinone. *Aniline*, when heated with it in acetic acid solution, forms naphthoquinone di-anilide.

Its dihydride is described as AMIDO-NAPHTHO-HYDROQUINONE.

AMIDO NAPHTHOQUINONE-IMIDE $C_{10}H_8N_2O$ *i.e.* $C_{10}H_5(NH_2)\langle{}^{NH}_{O}$.

Di-imido-naphthol. From di-amido-(α)-naphthol and Fe_2Cl_6Aq (Graebe a. Ludwig, *A.* 154, 307). Minute needles, v. sl. sol. cold water, v. sol. alcohol. Boiling alkalis and dilute acids at 120° convert it into oxy-naphthoquinone. Reducing agents produce di-amido-(α)-naphthol. Aniline heated with its hydrochloride forms naphthoquinone di-anilide. Salt.—B'HCl: dark red monoclinic prisms with green lustre $a:b:c = 2{\cdot}967:1:2{\cdot}396$ $\beta = 74°\ 28'$ — $B'_2H_2PtCl_6$. — $B'H_2CrO_4$: S. ·13 at 12°.—$B'H_2SO_4$.

Bromine-water added to an aqueous solution of amido-naphthoquinone imide produces two derivatives (Kronfeld, *B.* 17, 715):

1. $C_9H_4Br_2O_2$ [173°]: white plates, sol. alcohol, benzene, HNO_3 (S.G. 1·4), and $CHCl_3$.
2. $C_{10}H_6Br_3NO_3$ *i.e.* $CBr_3.CO.C_6H_4.C(NH).CO_2H$ [213°]: white needles, sol. alcohol, benzene and HNO_3 (S.G. 1·4), insol. chloroform. It is split up by cold *alkalis* into phthalimide and bromoform. When heated alone or better with H_2SO_4 at 140° it gives CO_2, Br_2 and an acid $C_9H_6Br_2NO$ [237°]. This loses HBr when boiled for a long time with alkalis. When heated with H_2SO_4 it gives phthalic acid.

AMIDO-NAPHTHOQUINONE SULPHONIC ACID $C_{10}H_8N_2SO_4$. Minute coppery needles, formed by oxidising di-amido-naphthol sulphonic acid.

DI-AMIDO-DINAPHTHYL $C_{20}H_{16}N_2$. *Dinaphthyline.* $C_{10}H_6(NH_2).C_{10}H_6(NH_2)$. [273°]. Colourless plates (from benzene). Formed together with a smaller quantity of the isomeric naphthidine by warming (αα)-hydrazonaphthalene with two mols. of dilute HCl at 70°–80°; a clear solution is formed from which the naphthidine is ppd. as its sparingly soluble hydrochloride by adding an excess of HCl, the easily soluble hydrochloride of dinaphthyline remaining in solution.

Reactions.—By diazotising and boiling with alcohol it is converted into (αα)-dinaphthyl [154°]. By boiling with acids NH_3 is easily split off, giving imido-dinaphthyl $\begin{matrix}C_{10}H_6\\|\\C_{10}H_6\end{matrix}\rangle NH$. By CrO_3 it is oxidised to phthalic acid.

Salts. — $B''H_2Cl_2$*: easily soluble. — $B''H_2Cl_2PtCl_4$: sparingly soluble yellow plates (Nietzki a. Goll, *B.* 18, 5254).

Di-amido-dinaphthyl (*naphthidine*). Probably [4:1] $C_{10}H_6(NH_2).C_{10}H_6(NH_2)$ [1:4]. [198°]. Silvery plates or colourless tables. Soluble in alcohol and benzene. Formed, together with its isomeride dinaphthyline, in small quantity by heating (αα)-hydrazonaphthalene with HCl, and in large quantity by reduction of (αα)-azonaphthalene with $SnCl_2$ and HCl.

Preparation.—One pt. of azonaphthalene is dissolved in 45 pts. of hot acetic acid, and a solution of $SnCl_2$ (1 pt.) in 2 pts. of HCl and 2–3 pts. of water is added in sufficient quantity to decolourise it; on adding an excess of HCl the sparingly soluble hydrochloride of naphthidine is ppd.

Reactions.—Fe_2Cl_6, CrO_3, Cl_2, &c., produce a carmine red colouration or pp. with solutions of naphthidine salts. By heating with CrO_3 it is oxidised to (α)-naphthoquinone and finally to phthalic acid. Its diazo-compound yields violet colouring-matters with the sulphonic acids of (β)-naphthol. By boiling the diazo-compound with alcohol it yields (αα)-dinaphthyl [154°].

Salts.—$B''H_2Cl_2$: sparingly soluble colourless silvery plates.—$B''H_2Cl_2PtCl_4$.—$B''H_2SO_4$: very sparingly soluble glistening plates.

Di-acetyl-derivative $C_{20}H_{12}(NHAc)_2$ [over 300°]; nearly insoluble in ordinary solvents (Nietzki a. Goll, *B.* 18, 3254).

Di-amido-(αα)-dinaphthyl $C_{20}H_{12}(NH_2)_2$. Obtained by reduction of di-nitro-dinaphthyl with zinc dust and HCl. It is readily oxidised to the di-imido-compound $C_{20}H_{12}\langle{}^{NH}_{NH}$, so that it cannot be diazotised. $B''H_2Cl_2$: easily soluble colourless needles. The bichromate pps. in brown crystals.

Di-acetyl-derivative $C_{20}H_{12}(NHAc)_2$. [Above 300°]. Colourless needles; insoluble in all solvents (Julius, *B.* 19, 2551).

Twenty-eight di-amido-(αα)-di-naphthyls are indicated by theory.

Tetra-amido-iso-di-naphthyl $C_{20}H_{10}(NH_2)_4$. [164°–167°]. From tetra-nitro-iso-di-naphthyl. Grey powder, sl. sol. alcohol, m. sol. toluene (Staub a. Watson Smith, *C. J.* 47, 104).

AMIDO-NITRO- *v.* NITRO-AMIDO-.

AMIDO-NITRO-BROMO- *v.* BROMO-NITRO-AMIDO-.

AMIDO-NITRO-CHLORO- *v.* CHLORO-NITRO-AMIDO-.

AMIDO-NITRO-IODO- *v.* IODO-NITRO-AMIDO-.

AMIDO-OCTOIC ACID $C_8H_{17}NO_2$ *i.e.* $C_6H_{13}.CH(NH_2).CO_2H$. *Amido-caprilic acid.* From heptoic aldehyde-ammonia (œnanthol-ammonia) and HCN (Erlenmeyer a. Sigel, *A.* 176, 341). Pearly white laminæ, v. sl. sol. alcohol, ether, and cold water. Neutral. Volatilises before fusing. Salts. — HA'HCl. — $HA'HNO_3$: slender needles. — $(HA')_2H_2SO_4$. — CuA'_2.

Nitrile $C_6H_{13}.CH(NH_2).CN$. [0°]. From HCN and œnanthol-ammonia (E. a. S.). Oil, miscible with alcohol and ether. Salts.—$C_8H_{16}N_2HCl$: satiny, six-sided plates.—$(C_8H_{16}N_2)_2H_2PtCl_6$.

Amide $C_6H_{13}.CH(NH_2).CONH_2$. From the nitrile and conc. HCl. Salts.—$(C_8H_{18}N_2O)_2H_2PtCl_6$.—$C_8H_{18}N_2OHCl$. Converted by aqueous $NaHCO_3$ into an acid, $C_9H_{18}N_2O_3$ (?).

AMIDO-OCTYL-BENZENE *v.* AMIDO-PHENYL-OCTANE.

AMIDO-OCTYL-TOLUENE *v.* AMIDO-TOLYL-OCTANE.

AMIDO-ŒNANTHYLIC ACID *v.* AMIDO-HEPTOIC ACID.

AMIDO-OPIANIC ACID *v.* OPIANIC ACID.

TRI-AMIDO-ORCIN $C_7H_{11}N_3O_2$ *i.e.* $C_6Me(OH)_2(NH_2)_3$. From tri-nitro-orcin by sodium-amalgam or by Sn and HCl. Its solutions readily oxidise in air, forming amido-di-imido-orcin (*q. v.*) (Stenhouse, *Pr.* 21, 125).

AMIDO-OXALOXYL-ACETIC ACID $CO_2H.CH(NH_2).CO.CO_2H$. *Phenyl hydrazide* $CO_2H.CH(NH_2).C(N_2HPh).CO_2H$. Obtained by reduction of an alkaline solution of the di-phenyl-hydrazide of di-oxy-tartaric acid $C_2(N_2HPh)_2(CO_2H)_2$ with sodium amalgam.

White pp., very oxidisable, its alkaline solution quickly becoming reddish-violet on contact with the air. By warming with H_2SO_4 it is converted into the anhydride $C_{10}H_9N_3O_3$ which is probably oxy-amido-quinizine-carboxylic acid (*q. v.*). By further reduction of the alkaline solution with sodium-amalgam di-amido-succinic acid [125°] is formed (Tafel, *B.* 20, 244).

AMIDO-OXINDOLE *v.* Oxindole.

AMIDO-OXY- *v.* Oxy-Amido-.

AMIDO-PHENANTHRENE *v.* Phenanthrene.

AMIDO-DI-PHENIC ACID $C_{14}H_{11}NO_4$ *i.e.* [1:2] $CO_2H.C_6H_4.C_6H_3(NH_2).CO_2H$ [1:5:2]. The hydrochloride, $H_2A''HCl$, obtained from nitro-di-phenic acid, forms silvery laminæ. When distilled with lime it produces *p*-amido-fluorene, $C_{13}H_9NH_2$ [123°] (Stasburger, *B.* 16, 2347).

***o*-Di-amido-di-phenic acid** $C_{14}H_{12}N_2O_4$ *i.e.* [3:2:1] $(CO_2H)(NH_2).C_6H_3.C_6H_3(NH_2)(CO_2H)$ [1:2:3]. Formed, by intramolecular change, when *o*-hydrazo-benzoic acid is boiled with HCl (Griess, *B.* 7, 1609).

***m*-Di-amido-di-phenic acid** $C_{14}H_{12}N_2O_4 1\frac{1}{2}aq$ *i.e.* [2:4:1] $(CO_2H)(NH_2).C_6H_3.C_6H_3(NH_2)(CO_2H)$ [1:4:2]. *Benzidine di-carboxylic acid.*

Formation.—1. From the corresponding di-nitro-compound (Hummel, *A.* 193, 128; Struve, *B.* 10, 75; Schultz, *B.* 12, 235).—2. From *m*-hydrazo-benzoic acid by boiling with HCl (G.).

Properties.—Short needles (from water); v. sl. sol. water, alcohol, and ether. It gives benzidine and di-amido-fluorene when distilled with lime.

Salts. — $Ag_2A''aq$. — $H_2A''2HCl$. — $H_2A''2HNO_3$.—$H_2A''H_2PtCl_6$ 2aq.

AMIDO-PHENOL.

***o*-Amido-phenol** C_6H_7NO *i.e.* $C_6H_4(NH_2)(OH)$ [1:2]. [170°]. S 1·7 at 0° (Körner).

Formation.—1. By reducing *o*-nitro-phenol (Hofmann, *A.* 103, 351; Fritzsche, *A.* 110, 166; Schmitt a. Cook, *K.* 3, 62).

Properties.—Scales; may be sublimed.

Salts.—B'HCl; S. ·8 at 0°.—$B'_2H_2SO_4$.

Reactions.—1. *Oxidised* by K_3FeCy_6 forming a dye ($C_{24}H_9N_3O_2$?) which sublimes as pink needles (G. Fischer, *J. pr.* [2] 19, 319).—2. *Nitrous acid* forms *o*-diazo-phenol. — 3. Converted into oxy-quinoline by heating with *glycerin*, *o-nitro-phenol*, and H_2SO_4 (Skraup, *B.* 15, 893).—4. *Lactic acid*, *o-nitro-phenol* and H_2SO_4 give oxy-methyl-quinoline (oxy-quinaldine).—5. $CH_2Cl.CO_2H$ gives oxy-phenyl-amido-acetic acid, $CO_2H.CH_2.NH.C_6H_4.OH$ (Vater, *J. pr.* [2] 29, 286). — 6. $Cl.CO_2Et$ gives oxy-phenyl-carbamic ether, $HO.C_6H_4.NH.CO_2Et$, [86°], which is converted by distillation into alcohol and oxy-methenyl-amido-phenol $C_6H_4{<}{}^{N}_{O}{>}C.OH$, [138°] (Grönvick, *Bl.* [2] 25, 178).—7. *Potassic xanthate* converts the hydrochloride of amido-phenol into sulpho-carbanil $C_6H_4{<}{}^{N}_{O}{>}CSH$, called also thio-carbamido-phenol and 'oxy-phenyl-thio-carbimide' (Kalckhoff, *B.* 16, 1825; Zincke a. Hebebrand, *A.* 226, 60).—8. Amido-phenol (30 g.) heated with alcoholic *quinone* (43 g.) forms hydroquinone; and, on cooling, violet needles of a *base* $C_{24}H_{18}N_4O_4$ [250°] separate. This base is soluble in aniline, sparingly soluble in alcohol, benzene, and chloroform. In dilute acids it forms deep red solutions. Boiled with NaOH, ammonia comes off and *o*-amido-phenol and other products are formed. The salts of the base have green metallic lustre and are easily soluble in alcohol but sparingly soluble in water; much water decomposes them into acid and base.—B''2HCl.—B''2HClPtCl₄.—$B''_2H_2SO_4$. Acetyl derivative $C_{24}H_{16}Ac_2N_4O_4$. [285°]. Oxidised in glacial acetic acid solution by HNO_3, this gives $C_{25}H_{15}N_5O_6$ [275°-280°]. Benzoyl derivative $C_{24}H_{16}Bz_2N_4O_4$. [265°]. *Reactions.*—*Nitrous acid* converts the base into $C_{24}H_{10}N_6O_6$, which forms small red needles, [above 290°]. HNO_3 oxidises it in acetic acid solution to a body which crystallises in yellow needles [260°] (Zincke a. Hebebrand, *A.* 226, 60).

Acetyl derivative $C_6H_4(OH)(NHAc)$. [201°]. From its anhydro-derivative by boiling with dilute H_2SO_4 (Ladenburg, *B.* 9, 1525). According to Morse (*B.* 11, 232) it can be formed by reducing *o*-nitro-phenol with Sn and HOAc (*cf.* Zincke a. Hebebrand, *A.* 226, 69). Glittering white plates, v. sol. alcohol and hot water; sol. KOHAq. Not affected by quinone.

Anhydro derivative $C_6H_4{<}{}^{O}_{N}{>}C.CH_3$.

Ethenyl-o-amido-phenol. [201°]. S.G. $\frac{0}{}$ 1·1365. Formed by heating *o*-amido-phenol with Ac_2O, or its acetyl derivative with P_2O_5 (L.).

Benzoyl derivative $C_6H_4(NHBz)(OH)$. [167°]. From the anhydro-compound by boiling with aqueous acids, or from the di-benzoyl derivative by boiling with water and $BaCO_3$ (Hübner, *A.* 210, 387; Bottcher, *B.* 16, 629). Laminæ, sl. sol. cold water, v. sol. hot water, sol. alcohol, ether, and benzene.

Anhydro derivative $C_6H_4{<}{}^{O}_{N}{>}C.Ph$.

Benzenyl-o-amido-phenol. [103°]. (314°). Formed by heating *o*-amido-phenol with BzCl, HOBz, or phthalic anhydride, and distilling the product (L.); or by reducing *o*-nitro-phenyl benzoate, with Sn and HCl. It is insol. water, v. sol. alcohol. Its salts are unstable, but $B'_2H_2PtCl_6$ may be crystallised from alcohol.

Di-benzoyl derivative $C_6H_4(NHBz)(OBz)$. [176°]. From *o*-amido-phenol hydrochloride and BzCl (Hübner, *A.* 210, 387).

Formyl derivative. Only known in its

Anhydro-derivative $C_6H_4{<}{}^{O}_{N}{>}CH$.

Methenyl-amido-phenol. [31°]. (183°). Formed by heating *o*-amido-phenol with formic acid.

Phthalyl derivative $C_6H_4{:}(C_2O_2){:}N.C_6H_4.OH$. *Oxy-phenyl-phthalimide.* [220°]. From *o*-amido-phenol and phthalic anhydride at 220°. Yellowish prisms; converted by heat into CO_2 and anhydro-benzoyl-*o*-amido-phenol, and by boiling Na_2CO_3Aq into phthaloxyl-amido-phenol, $CO_2H.C_6H_4.CO.NH.C_6H_4OH$, [223°] (Ladenburg, *B.* 9, 1528).

Methyl derivative $C_6H_4(NH_2).OMe$. *o-Anisidine* (228°). From *o*-nitro-anisol by reduction (Brünck, *Z.* 1867, 205; Mühlhäuser, *B.* 13, 919, *A.* 207, 235; Herold, *B.* 15, 1684). Liquid. It acts upon quinone thus:

$$3C_6H_4O_2 + 2C_6H_4(OMe)NH_2 =$$
$$2C_6H_4(OH)_2 + C_6H_2O_2(C_6H_3(OMe)NH_2)_2.$$

The product forms reddish-violet needles (from glacial HOAc and benzene), [230°], and gives a fine blue solution in conc. H_2SO_4 (Zincke, *A.*

226, 68). **Salts.**—B'HCl: needles (from alcohol); may be sublimed.—B'HBr.—$B'H_2SO_4$.—$B'_2H_2PtCl_6$.—Chloroacetate (Vater, *J. pr.* [2] 29, 288). Acetyl derivative.—$C_6H_4(NHAc).OMe$. [84°] (204°). Pearly crystals. Sol. hot water. Benzoyl derivative. — $C_6H_4(NHBz).OMe$ [59°].

Ethyl derivative $C_6H_4(NH_2).OEt$. *o-Amido-phenetol.* (229°). A liquid prepared by reducing *o*-nitro-phenetol (M. Förster, *J. pr.* 129, 344). Reactions.—1. *Bromine* forms a di- and a tri-bromo-derivative. — 2. *Cyanogen chloride* passed into an ethereal solution forms ethoxy-phenyl cyanamide, [94°], *o*-amido-phenetol hydrochloride being ppd.:

$$2C_6H_4(NH_2).OEt + CNCl =$$
$$C_6H_4(NH_2)OEtHCl + C_6H_4(NH.CN).OEt$$

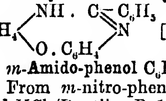
(Berlinerblau, *J. pr.* [2] 30, 98). *Chloroacetate.*—$C_6H_4(NH_2)(OEt)CH_2Cl.CO_2H$ (Vater, *J. pr.* [2] 29, 288).

Ethylene derivative $C_2H_4(O.C_6H_4.NH_2)_2$. [128°]. By reducing the ethylene ether of nitro-phenol with Sn and HCl. *Properties.*—Trimetric plates (from alcohol or water). Feels greasy. Insoluble in cold water, soluble in alcohol, ether, chloroform and benzene. Forms a bluish-black solution with H_2SO_4. Fe_2Cl_6 gives a sepia-brown colour. $K_2Cr_2O_7$ and HCl give a brownish-red colour (E. Wagner, *J. pr.* [2] 27, 201). Salts. — B''2HCl2aq. Silver-grey glittering flat needles grouped in tufts (from water). The acetate is extremely soluble. The sulphate is the least soluble salt, it crystallises in pearly plates but, like the oxalate, it readily becomes oxidised. Diacetyl derivative.—[226°]. Needles.

Oxethyl derivative.— $HO.C_2H_4.O.C_6H_4.NH_2$. [90°]. Got by reducing $BzO.C_2H_4.O.C_6H_4.NO_2$ (*v.* o-Nitro-phenol) by Sn and HCl (Weddige, *J. pr.* 132, 252). *Properties.*—Colourless plates, slightly soluble in water, readily soluble in alcohol, ether and boiling benzene. A feeble base. Benzoyl derivative $BzO.C_2H_4.O.C_6H_4.NH_2$ [c. 100°]. Got by reducing the benzoyl derivative of the oxethyl ether of *o*-Nitro-phenol (*q. v.*).

Amido-ethyl derivative $NH_2.C_2H_4.O.C_6H_4.NH_2$

Anhydro-benzoyl derivative



[151°] *v.* o-Nitro-phenol.

***m*-Amido-phenol** $C_6H_4(NH_2)(OH)$ [1:3].

From *m*-nitro-phenol by reducing with Sn and HCl (Bantlin, *B.* 11, 2106). The free base is extremely unstable. Its hydrochloride, B'HCl, is formed by reducing bromo-*m*-nitro-phenol (Pfaff, *B.* 16, 613).

Methyl derivative $C_6H_4(NH_2)(OMe)$ *m-Anisidine* (251°). Salt.—B'HCl (Pfaff).

Ethyl derivative $C_6H_4(NH_2)(OEt)$. (180°–205°) at 100 mm. From the nitro compound by Sn and HCl (P. Wagner, *J. pr.* [2] 32, 71). A yellowish liquid, turning red in air. Salts.—$B'_2H_2SnCl_4$: plates.—B'HCl: silky grey needles; insol. ether, sol. water and alcohol. — $B'_2H_2SO_4$ 1½aq.—*$B'_2H_2C_2O_4$: brownish plates.—*B'HBr (Staedel, *B.* 16, 29). Acetyl derivative $C_6H_4(NHAc)(OEt)$. [97°]. Glittering white plates (from water).

Ethylene derivative $C_2H_4(O.C_6H_4NH_2)_2$. [135°]. Obtained by reducing the corresponding nitro-compound. Short prisms (from alcohol). Sl. sol. hot water, sol. hot alcohol and benzene, sl. sol. ether. Forms crystalline salts.

***p*-Amido-phenol** $C_6H_4(NH_2)(OH)$ [1:4]. [170°] (S. a. C.). [c. 184°] (L.). S. 1·1 at 0°. S. (alcohol) 4·5 at 0°.

Preparation.—1. From *p*-nitro-phenol by reducing with iron and acetic acid (Fritzsche, *A.* 110, 166) or Sn and HCl (Schmitt a. Cook, *Z.* 3, 61).—2. From amido-salicylic acid by distillation (Schmitt, *B.* 1, 67).—3. From nitroso-phenol (Baeyer a. Caro, *B.* 7, 965).

Properties.—Crystalline, but very unstable. May be sublimed (S. a. C.). In capillary tubes it turns brown at 140° and melts at 184° with decomposition (Lossen, *A.* 175, 296).

Salts.—B'HCl. S. 71 at 0°. S. (alcohol) 10. Turns brown in air.—B'HOAc. [183°]. S. 11 at 0°. S. (alcohol) 8·3 at 0°.

Reactions.—1. *Bleaching powder solution* added to a cold solution of *p*-amido-phenol hydrochloride forms quinone chloro-imide, but if added to a hot concentrated solution of the salt it forms a mixture of tri- and tetra-chloro-quinones.—2. *Bleaching powder* added to a solution of *p*-amido-phenol in fuming HCl at 0° forms pure tri-chloro-quinone.—3. *Chlorine gas* passed in excess into a solution of *p*-amido-phenol in fuming HCl forms pure tri-chloro-amido-phenol (Schmitt a. Andresen, *J. pr.* 131, 435). The observation that chlorine converts *p*-amido-phenol hydrochloride in aqueous solution into quinone-chloro-imide, while in presence of conc. HCl chlorine converts *p*-amido-phenol into tri-chloro-amido-phenol, is explained by the fact that quinone-chloro-imide is changed by conc. HCl into chloro-*p*-amido-phenols. In this decomposition the first reaction is:

$$C_6H_4{<}^{O}_{NCl} + 4HCl = C_6H_4{<}^{OH}_{NH_2,HCl} + 2Cl_2.$$

This reaction is similar to that between chloride of nitrogen and HCl:

$$NCl_3 + 4HCl = NH_4Cl + 3Cl_2.$$

Hence both ammonia and amidogen are protected by conc. HCl from the action of chlorine. 4. Acts on *quinone* as follows:

$$3C_6H_4O_2 + 2NH_2.C_6H_4OH =$$
$$2C_6H_4(OH)_2 + C_6H_2(NH.C_6H_4.OH)_2O_2.$$

It is best to use the hydrochloride of *p*-amido-phenol in hot aqueous solution; the product, which separates on cooling, is sparingly soluble in the usual menstrua, and does not melt below 290° (Zincke a. Hebebrand, *A.* 226, 70).—5. HCl, $NaNO_2$, and K_2SO_3 produce *p*-diazo-phenol sulphite, $HO.C_6H_4.N_2.SO_3H$ (Reisenegger, *A.* 221, 316).—6. $Cl.CO_2Et$ forms *p*-oxy-phenyl-carbamic ether, $HO.C_6H_4.NH.CO_2Et$ [120°].—7. A mixture of HCl and *potassium cyanate* produces *p*-oxy-phenyl-urea, $HO.C_6H_4.NH.CO.NH_2$ [168°].—8. HCl and *potassium sulphocyanide* produce, when the solution is evaporated, *p*-oxy-phenyl-thio-urea, $HO.C_6H_4.NH.CS.NH_2$ [214°].—9. CS_2 produces di-oxy-di-phenyl-thio-urea, $CS(NH.C_6H_4.OH)_2$.

Acetyl derivative $C_6H_4(NHAc)(OH)$. [179°]. Large white prisms; obtained by reducing *p*-nitro-phenol with tin and glacial acetic acid (Morse, *B.* 11, 232).

Benzoyl derivative $C_6H_4(NHBz)(OH)$. [227°]. From *p*-amido-phenol and BzCl

(Hübner, *A.* 210, 378). Needles, insol. water, alcohol, and petroleum, sl. sol. hot alcohol.

Amido-phenyl benzoate $C_6H_4(NH_2)(OBz)$. [154°]. Obtained by reducing *p*-nitro-phenyl benzoate. Plates; sol. boiling alcohol, and water, v. e. sol. glacial acetic acid.

Di-acetyl derivative $C_6H_4(NHAc)(OAc)$ [151°]. From *p*-amido-phenol and Ac_2O.

Di-benzoyl derivative $C_6H_4(NHBz)(OBz)$. [231°]. From *p*-amido-phenol and BzCl.

Methyl derivative $C_6H_4(NH_2)(OMe)$. *p-Anisidine*. [56°]. (246°). From *p*-nitro-anisol (Brunk, *Z.* 1867, 205; Salkowski, *B.* 7, 1009). Formed also, together with CO_2, when anisoyl-hydroxylamine is distilled (Lossen, *A.* 175, 296). Tables (from water). B'HCl: long needles. $B'_2H_2PtCl_6$.

Ethyl derivative $C_6H_4(NH_2).OEt$. (253°). Obtained by reducing *p*-nitro-phenetol (Halloch, *B.* 14, 37).

Ethylene derivative $C_2H_4(O.C_6H_4NH_2)_2$ [c. 170°]. By reducing the ethylene ether of *p*-nitro-phenol (*q. v.*). *Properties.*—Needles, which turn brown in the air. Crystallises from alcohol or from water. Very soluble in hot benzene, less soluble in $CHCl_3$ or ether. Forms a deep blue colour with $K_2Cr_2O_7$ and HCl. Fe_2Cl_6 gives a cherry red (E. Wagner, *J. pr.* [2] 27, 206). Salt.—B''2HCl: long thin needles grouped concentrically. The acetate is deliquescent. The sulphate is the least soluble salt. The oxalate is but slightly soluble.

(*a*) **Di-amido-phenol** $C_6H_3(OH)(NH_2)_2$ [1:2:4]. From (*a*) di-nitro-phenol (Gauhe, *A.* 147, 66; Stuckenberg, *B.* 10, 385; Post a. Stuckenberg, *A.* 205, 96). The free base is extremely unstable.

Salts.—B''2HCl. Precipitated by adding conc. HCl to its aqueous solution. Small prisms insoluble in conc. HCl, and in absolute alcohol. Dilute solutions are turned violet-red by Fe_2Cl_6 or bleaching powder (H. Köhler, *J. pr.* [2] 29, 270).—B''2HI.—$B''H_2SO_4$2aq: tables.

Di-benzoyl derivative $C_6H_3(NHBz)_2OH$ (?). [187°]. From the hydrochloride and BzCl. Pale red leaflets; sol. alcohol, chloroform, and aniline, sl. sol. ether, insol. water. Forms a nitro derivative [c. 169°].

Tri-benzoyl derivative $C_6H_3(NHBz)_2(OBz)$(?). [233°]. Rhombohedra, insol. alcohol, chloroform, and ether; sol. aniline.

(*β*) **Di-amido-phenol** $C_6H_3(NH_2)_2OH$ [2:6:1]. The free base is very unstable; its hydrochloride is got by reducing the corresponding di-nitro-phenol (Post a. Stuckenberg, *A.* 205, 79).

Salts.—B''2HCl: thick pointed prisms, v. sol. water, sl. sol. alcohol. $B''H_2SO_4$: yellow needles.

Di-benzoyl derivative $C_6H_3(NHBz)_2OH$. [209°-213°]. Minute crystals, sol. alcohol, sl. sol. benzene.

Tri-benzoyl derivative $C_6H_3(NHBz)(NBz_2)(OH)$. [184°]. Sol. warm Na_2CO_3Aq, insol. chloroform.

Tetra-benzoyl derivative $C_6H_3(NBz_2)(NBz_2)OH$. [182°]. Leaflets; insol. water, sol. warm Na_2CO_3Aq, alcohol, benzene, and ether.

Di-amido-phenol $C_6H_3(OH)(NH_2)_2$. [1:3:4].

Hydrochloride B''2HCl.—Formed by heating ethoxy-*p*-amido-phenyl carbamic ether, $C_6H_3(OH)(NH_2)NH.CO_2Et$ with fuming HCl (H. Köhler, *J. pr.* [2] 29, 269). Oblong plates. Very soluble in conc. HCl and in absolute alcohol. Dilute solutions are turned blood-red by Fe_2Cl_6 or bleaching powder.

Tri-amido-phenol $C_6H_2(NH_2)_3OH$. [2:4:6:1]

Formation.—1. From picric acid by reduction (Heintzel, *Z.* 1867, 338; *B.* 1, 111; Bamberger, *B.* 16, 2400).—2. From picramide, Sn and HCl (Hepp, *A.* 215, 350). The free base is unstable. The salts give a blue colour with a large quantity of water containing air. In conc. solution Fe_2Cl_6 gives deep blue glittering crystals of amido-di-imido-phenol (Heintzel).

Salts.—B'''3HCl.—$B'''_23H_2SO_4$.—$B'''H_3SnCl_6$ 1½aq.—$B'''HI H_2SO_4$2aq.—$B'''HIH_3PO_4$2aq.—$B'''_2H_4FeCy_6$. If the hydrochloride is boiled with HCl di-amido-dioxy-benzene is got (Salkowski, *A.* 174, 260).

Tri-acetyl derivative $C_6H_2(NHAc)_3OH$ [263°]. From the hydrochloride of tri-amido-phenol by heating with NaOAc and Ac_2O. White plates, soluble in acetic acid, hot alcohol, water, aqueous acids and alkalis, very sparingly in benzene and acetone; by HNO_3, CrO_3 or Fe_2Cl_6 it is oxidised to the tetra-acetyl derivative of tetra-amido-di-oxy-diphenyl-quinone

$C_6H(NHAc)_2(OH).O$
| | (Bamberger, *B.* 16, 2400).
$C_6H(NHAc)_2(OH).O$

Reaction.—Tri-amido-phenol hydrochloride is converted by bromine water into 'bromo-dichromazin' $C_{18}H_8N_3Br_{11}O_7$. This body separates from alcohol in yellow needles with feeble violet dichroism. Boiling dilute H_2SO_4 converts it into 'bromo-dichroic acid' $C_{18}H_7Br_{11}O_{11}$ and ammonia. Bromine converts bromodichromazin into hexa-bromo-acetone (Wedel a. Gruber, *B.* 10, 1137).

Tetra-amido-phenol

Ethyl-ether, hydrochoride $C_6H(NH_2)_4(OEt),2HCl$. By reducing the product of the action of HCl upon tri-nitro-ethoxy-phenyl urethane.—(1).$C_6H(NO_2)_3(OEt)(NH.CO_2Et) + HCl = CO_2 + EtCl + C_6H(NO_2)_3(OEt)NH_2$.

(2.) $C_6H(NO_2)_3(OEt)NH_2 + 9H_2 = C_6H(NH_2)_4OEt + 6H_2O$.

Properties.—Crystallises from dilute alcohol. Insoluble in absolute alcohol, very soluble in water. Does not melt at 360°. Reduces solutions of Au and Pt. A feebly acid solution gives with Fe_2Cl_6 or bleaching-powder the following succession of colours: dark-green, violet-red, reddish-brown, yellowish-brown, yellow, colourless.

AMIDO-PHENOL SULPHONIC ACID $C_6H_7NSO_4$ *i.e.* $C_6H_3(NH_2)(OH)HSO_3$. [2:1:4] S. 1 at 14°. Prepared by reduction of *o*-nitro-phenol-sulphonic acid or by sulphonation of *o*-amido-phenol. Large colourless crystals like calc-spar. Does not form salts.

Anilide $C_6H_3(NH_2)(OH)(SO_2.NHPh)$. [205°] Colourless needles; soluble in alcohol, acetic acid and benzene insoluble in ether.

Benzoyl derivative $C_6H_3(NHBz)(OH)(SO_3H)$. Salts.—NaA'4½aq: colourless needles, soluble in water a. alcohol.—BaA'_2; colourless spangles sparingly soluble.—$CaA'_2$4½aq: sparingly soluble colourless scales (Post a. Holst, *B.* 13, 617; *A.* 205, 49).

***p*-Amido-phenol sulphonic acid** $C_6H_3(OH)(NH_2)SO_3H$ [1:4:2]. S. ·07 at 14°.

Formation.—1. From *p*-amido-phenol hydrochloride and fuming H_2SO_4 (Post, *B.* 6, 397).—2. From *p*-nitro-phenol sulphonic acid (Post a. Holst, *B.* 13, 617).—3. Together with azoresorufin by heating a mixture of resorcin and nitrobenzene with H_2SO_4 (Brunner a. Krämer, *B.* 17, 1867).—4. From quinone chloro-imide and conc. Na_2SO_3 (Schmitt a. Bennewitz, *J. pr.* [2] 8, 7).

Properties.—White glistening needles; sl. sol. cold water, v. sl. sol. alcohol, insol. ether. Does not combine with acids, but forms metallic salts, *e.g.* $Ba(O.C_6H_3(NH_2)SO_3)$. Reduces cold ammoniacal $AgNO_3$. Turned violet by Fe_2Cl_6. Not ppd. by lead acetate.

Anilide $C_6H_3(OH)(NH_2)SO_2NPhH$. [98°]. Small colourless crystals; v. sol. alcohol, acetic acid, and benzene; insol. ether.

p-**Amido-phenol di-sulphonic acid** $C_6H_2(OH)(NH_2)(SO_3H)_2$ [1:4:2:6] (?). From benzene-azo-phenol tri-sulphonic acid (*q. v.*) by ammonium sulphide (Wilsing, *A.* 215, 236; Limpricht, *B.* 15, 1293). White silky needles. Deliquescent; sl. sol. alcohol, insol. ether. Solution gives with Fe_2Cl_6 a deep violet colour. Its alkaline solutions show blue fluorescence for a short time. Salts.—KHA″aq: slightly sol. cold water.—NH_4HA″aq.—PbA″aq.

o-**AMIDO-DIPHENYL** $C_{12}H_{11}N$ *i.e.* $C_6H_5.C_6H_4.NH_2$ [1:2]. [45°]. From *o*-nitro-diphenyl with tin and glacial acetic acid (Hübner a. Lüddens, *A.* 209, 351).

Salts.—B′HCl: needles.—$B'_2H_2PtCl_6$4aq.: orange leaflets.

p-**Amido-diphenyl** $C_6H_5.C_6H_4.NH_2$ [1:4]. *Xenylamine*; *Martylamine.* [49°]. (320°). Occurs in the high-boiling fractions in the preparation of aniline (Hofmann, *Pr.* 12, 389; G. Schultz, *A.* 174, 212; Osten, *B.* 7, 171). Prepared by reducing *p*-nitro-diphenyl with tin and HCl (Hübner a. Osten, *A.* 209, 339). Colourless leaflets, sol. hot water, alcohol, and chloroform.

Salts.—B′HCl: leaflets.—$B'_2H_2PtCl_6$2aq; yellow leaflets, sl. sol. alcohol.—B′HNO_3: pearly leaflets.—$B'_2H_2SO_4$: leaflets, v. sl. sol. water, sl. sol. alcohol.—$B'_2H_2C_2O_4$: long needles, sol. water and alcohol.

Acetyl derivative $C_6H_5.C_6H_4.NAcH$. [167°]. Long needles; v. sl. sol. water.

Benzoyl derivative $C_6H_5.C_6H_4.NBzH$. [230°]. Leaflets; insol. water, v. sl. sol. alcohol.

Formyl derivative $C_6H_5.C_6H_4.NH.CHO$. [172°]. Prepared by heating *p*-amido-diphenyl with ethyl formate at 100°. Minute needles; sol. ether, sl. sol. alcohol, v. sl. sol. water (Zimmermann, *B.* 13, 1967).

p-**Amido-diphenyl sulphonic acid** $C_{12}H_8(NH_2)SO_3H$. [above 300°]. Formed by sulphonation of *p*-amido-diphenyl (Carnelley a. Schlevelman, *C. J.* 49, 380). Insol. water.

Salts.—NaA′2aq: colourless needles, m. sol. water.—$BaA'_2$4aq; v. sl. sol. water.

o-p-**Di-amido-diphenyl** $C_{12}H_{12}N_2$ *i.e.* [1:2] $NH_2.C_6H_4.C_6H_4.NH_2$ [1:4]. *Iso-benzidine.* (β)- or (δ)-*Di-amido-di-phenyl.* *Diphenyline.* [45°]. (363°) (Schultz, *A.* 207, 348).

Formation.—1. From *o*-nitro-*p*-amido-diphenyl (Schultz, *B.* 9, 548; 14, 612).—2. From di-amido-diphenyl carboxylic acid (Strasser a. Schultz, *A.* 210, 193).

Preparation.—An alcoholic solution of azobenzene (100 g.) is heated with a solution of $SnCl_2$ in conc. HCl; the liquid is evaporated to dryness, the residue dissolved in water and benzidine is ppd. as sulphate (100 g.) while *o-p*-di-amido-diphenyl sulphate (30 g.) remains in solution (Schmidt a. Schultz, *B.* 12, 482).

Properties.—Long needles, v. sl. sol. water.

Salts.—B″HCl: laminæ.—B″2HCl: needles.—B″H_2SO_4: prisms.—$B''_2H_2SO_4$.

Di-acetyl derivative $C_{12}H_{10}Ac_2N_2$. [202°].

m-m-**Di-amido-diphenyl** [1:3] $NH_2.C_6H_4.C_6H_4.NH_2$ [1:3]. From the nitro compound (Brunner a. Witt, *B.* 20, 1028). Crystals, sl. sol. water.—B″H_2SO_4.—B″H_2PtCl_6.

Di-acetyl derivative. [258°]. Long needles.

p-p-**di-Amido-diphenyl.** *Benzidine.* [1:4] $NH_2.C_6H_4.C_6H_4.NH_2$ [1:4]. *Xenylene-diamine.* [122°]. (above 360°).

Formation.—1. By the reduction of azobenzene or of azoxybenzene in alcoholic solution by SO_2 (Zinin, *A.* 85, 328).—2. From azobenzene by $SnCl_2$ and HCl (*v. sup.*).—3. By heating azobenzene with fuming HCl (Zinin, *A.* 137, 376), HBr (Werigo, *A.* 165, 202), or HI (Senziuk, *Z.* 1870, 267) in sealed tubes.—4. By reducing nitro-benzene with sodium-amalgam in presence of acetic acid, the product being treated with H_2SO_4 (Werigo, *A.* 135, 176).—5. From nitro-benzene, alcoholic NaOH, and zinc dust and subsequent treatment with acid (Alexejeff, *Z.* 1867, 497).—6. From di-amido-diphenic acid by distilling with BaO (Schultz, *A.* 196, 29).—7. From *p*-amido-*p*-nitro-diphenyl by Sn and HCl (Fittig, *A.* 124, 276).—8. From *p-p*-di-nitro-phenyl by tin and HCl (Schultz, *A.* 174, 227).—9. From hydrazo-benzene by treatment with mineral acids:

$C_6H_5.NH.NH.C_6H_5 = NH_2.C_6H_4.C_6H_4.NH_2$.

Preparation.—*V. o-p-di*-AMIDO-DIPHENYL.

Properties.—Silvery scales; may be sublimed. Sol. hot water, v. sl. sol. cold water, v. e. sol. alcohol and ether.

Salts.—B″H_2SO_4: small scales, v. sl. sol. water and alcohol.—B″2HCl: laminæ, v. sol. water and alcohol.—B″HCl: long needles, sl. sol. water; ppd. when a large excess of water is added to the preceding salt.—B″2HNO_3: four-sided laminæ, sol. hot water.—$B''_2H_2C_2O_4$: groups of silky needles, m. sol. water and alcohol.—B″$C_4H_6O_6$: laminæ; sol. water.

Reactions.—1. Even very dilute solutions give with *potassic bichromate* a deep blue pp. (Julius, *M.* 4, 193).—2. K_3FeCy_6 gives a blue pp.—3. *Chlorine-water* gives a blue colour soon becoming red.—4. Exhaustive *chlorination* with $SbCl_5$ gives per-chloro-diphenyl and per-chloro-benzene (Merz a. Weith, *B.* 16, 2874).—5. If very dilute *bromine-water* be poured upon a solution of benzidine in CS_2 the upper layer becomes blue, excess of bromine destroys this colour, the lower layer then turning red (Claus a. Risler, *B.* 14, 83).

Acetyl derivative $NH_2.C_6H_4.C_6H_4.NAcH$. [199°]. Needles, sl. sol. water.

Diacetyl derivative $NHAc.C_6H_4.C_6H_4.NAcH$. [317°]. Nearly insoluble in all solvents.

Di-formyl derivative $C_{12}H_8(NHCOH)_2$: crystalline powder, sublimable, insoluble in all ordinary solvents except nitrobenzene. Formed

by heating hydrazobenzene or benzidine with formic acid.

Di-benzoyl derivative $C_{12}H_8(NHBz)_2$: colourless needles or pearly plates; insol. alcohol, ether, and aniline; sol. nitrobenzene. Formed by heating hydrazobenzene or benzidine with BzCl (Stern, *B.* 17, 379).

Di-phthalyl derivative $C_{28}H_{16}N_2O_4$ [above 360°]: silky yellow needles, sol. hot nitro-benzene; insol. most other solvents. Formed by heating benzidine & hydrazobenzene with phthalic anhydride (Bandrowski, *B.* 17, 1181).

Oxalyl derivative $(C_6H_4.NH)_2C_2O_2$. An insoluble powder, obtained by heating benzidine oxalate at 200°.

Benzidine-v-sulphonic acid $H_2N.C_6H_4.C_6H_4.NH.SO_3H$. Formed by heating an alcoholic solution of azobenzene with hydric ammonium sulphite (Spiegel, *B.* 18, 1481).

Gelatinous pp. It gives colourless crystalline salts.

The HSO_3 is readily split off with production of benzidine by dissolving the acid in strong H_2SO_4.

Benzidine sulphonic acid (?)
$C_6H_4(NH_2).C_6H_3(NH_2)(SO_3H)$ (?). *Hydrazo-benzene sulphonic acid* $C_6H_5.NH.NH.C_6H_4.SO_3H$ (?). Ppd. by adding HCl to the product of the action of H_2S on an ammoniacal solution of azo-benzene sulphonic acid (Griess, *A.* 154, 213).—Yellow needles or plates (from water).—BaA'_2: plates. The free acid is decomposed by solution in aqueous NH_3 into benzidine and H_2SO_4. The above azobenzene sulphonic acid is converted by potash-fusion into *p*-oxy-azobenzene, and would therefore appear to be a *p*-sulphonic acid; in which case it is not clear how the conversion into a benzidine derivative could be effected. If, however, the acid is hydrazo-benzene sulphonic acid, we must assume that the benzidine transformation here takes place in alkaline solution, by displacement of SO_3H. In any case the removal of SO_3H by ammonia is peculiar.

Benzidine sulphonic acid
$C_{12}H_{11}N_2(SO_3H)\,2\frac{1}{4}$aq. Obtained by heating (α)-benzidine disulphonic acid with water at 210° (Limpricht, *B.* 11, 1048). Yellow needles (from alcohol); v. sol. water.—$KA'4$aq.—$BaA'_2 4$aq.—$PbA'_2 3$aq.

Chloride $C_{12}H_{11}N_2(SO_2Cl)$ [above 210°].

Benzidine disulphonic acid
[4:3:1]$C_6H_3(NH_2)(SO_3H).C_6H_3(SO_3H)(NH_2)$[1:3:4] S. ·08 at 22°. From azo-, or azoxy-, benzene disulphonic acid by reduction with $SnCl_2$, sodium-amalgam, or NaOH and zinc dust, followed by treatment with a mineral acid (Mährenholtz a. Gilbert, *A.* 202, 337; Brunnemann, *A.* 202, 344; Limpricht, *B.* 14, 1359). Monoclinic prisms (with 3aq). Dilute HCl at 230° gives benzidine and H_2SO_4. Nitrous acid diazotises this acid.—$Na_2A''3\frac{1}{2}$aq.—$K_2A''1\frac{1}{2}$aq.—$CaA''4$aq.—$BaA''4$aq.—$PbA''4$aq.

Benzidine di-sulphonic acid
$C_{12}H_6(NH_2)_2(SO_3H)_2$. From benzidine and fuming H_2SO_4 at 170°. Small white plates; v. sl. sol. water, insol. alcohol and ether (Griess, *B.* 14, 300). Salts.—$BaA''5$aq: white plates.—$BaA''2$aq: needles.—$^{x}Ag_2A''$: white crystalline pp.

Benzidine (α)-di-sulphonic acid
$C_{12}H_{10}N_2(SO_3H)_2$. *Hydrazo-benzene di-sulphonic acid (?).* Prepared by reducing potassium azo benzene (α)-di-sulphonate with $SnCl_2$ (Limpricht *B.* 14, 1357). Tables (containing 2aq); sl. sol cold water, v. sl. sol. alcohol.—$K_2A''3$aq.—BaA''aq.—$^{x}Ag_2A''$: white pp.—PbA'': needles sl. sol. cold, v. sol. hot, water.

Benzidine tetrasulphonic acid
$C_{12}H_4N_2(SO_3H)_4$. Prepared by sulphonation of the preceding with fuming H_2SO_4.—$Ba_2A''''14$aq: large prisms, v. sol. hot water, sl. sol. alcohol.—$^{x}K_4A''''$ (Limpricht, *B.* 14, 1513).

Other sulphonic acids of benzidine
Benzidine heated with a large excess of fuming H_2SO_4 above 170° forms a mixture of di-, tri-, and tetra-, sulphonic acids, and di-amido-diphenylene sulphone sulphonic acids (Griess, *B.* 18, Ref. 88).

Benzidine di-carboxylic acid *v. di*-AMIDO-DIPHENIC ACID.

Benzidine tetra-carboxylic anhydride

$$O\!<\!\substack{CO\\CO}\!>\!C_6H_2(NH_2).C_6H_2(NH_2)\!<\!\substack{CO\\CO}\!>\!O.$$

[above 360°]. Formed by the action of an HCl solution of $SnCl_2$ on azo-benzene tetra-carboxylic acid (azo-phthalic acid). Light-yellow tasteless powder. Insol. water, alcohol, ether, or dilute acids.

With alkalis it gives anhydride salts:—
$C_{12}H_8N_2(C_2O_3)(CO_2K)_2 5$aq: large prisms.
$C_{12}H_8N_2(C_2O_3)(CO_2Na)_2$aq: small needles.
$C_{12}H_8N_2(C_2O_3)(CO_2Ag)_2$: fine powder.
$C_{12}H_8N_2(C_2O_3)(CO_2)_2Pb$: amorphous powder.
$C_{12}H_8N_2(C_2O_3)(CO_2NH_4)(CO_2H)$: transparent prisms (Claus a. Hemmann, *B.* 16, 1759).

Di-amido-diphenyl $C_{12}H_{12}N_2$. *Iso-benzidine.* [125°]. Occurs among the products obtained by passing aniline through a red-hot tube (Bernthsen, *B.* 19, 420). White iridescent plates, sl. sol. water. Its aqueous solution gives no colouration with *potassic ferricyanide*, and a greyish-brown pp. with *chlorine water*. The solid base is turned greenish-black by strong HNO_3. The *sulphate* is sparingly soluble.

Tetra-amido-diphenyl
[3:4:1] $(NH_2)_2C_6H_3.C_6H_3(NH_2)_2$ [1:3:4]. Obtained by reducing di-nitro-*p*-*p*-di-amido-diphenyl (Brunner a. Witt, *B.* 20, 1025). Silvery plates.

α-AMIDO-PHENYL-ACETIC ACID $C_8H_9NO_2$ *i.e.* $C_6H_5.CH(NH_2).CO_2H$. Phenyl-amido-acetic acid. [256°]. Formed by heating α-bromo-phenyl-acetic acid with NH_3Aq (S.G. ·9) at 100° (Stöckenius, *B.* 11, 2002); or by saponifying its nitrile, obtained by the action of alcoholic NH_3 on the cyanhydrin of benzoic aldehyde (Tiemann a. Friedländer, *B.* 14, 1967). White leaflets or prisms; may be sublimed. Sl. sol. cold water, m. sol. hot water. It forms unstable salts with bases, but more stable salts with acids, though these are decomposed by water. Distilled with lime, it gives benzylamine (Tiemann, *B.* 13, 383).

Salts.—$B'HCl$: trimetric prisms.—$B'HNO_3$.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.—AgA': prisms, v. sl. sol. water.—BaA'_2: small white plates; v. sol. hot water.—$MgA'_2\frac{1}{2}$aq: plates, sl. sol. water.

Amide. The hydrochloride forms thick prisms, sl. sol. alcohol.

Nitrile $C_6H_5.CH(NH_2).CN$. Yellow oil (*v. sup.*).

m-Sulphonic acid
$C_6H_4(SO_3H).CH(NH_2).CO_2H$. Minute needles; sl.

sol. cold water, insol. ether (Plöchl a. Loë, *B.* 18, 1182).

o- **Amido-phenyl-acetic acid.** When *o*-nitro-phenyl-acetic acid is reduced the product is not *o*-amido-phenyl-acetic acid but its anhydride, oxindol (*q. v.*) (Baeyer, *B.* 11, 583).

m-**Amido-phenyl-acetic acid** $C_6H_4(NH_2).CH_2.CO_2H$ [1:3]. [148°]. Formed by reducing *m*-nitro-phenyl-acetic acid (Gabriel a. Bergmann, *B.* 16, 2065).

Nitrile $C_6H_4(NH_2).CH_2.CN$. *m- Amido-benzyl cyanide.* A liquid obtained by reducing *m*-nitro-phenyl-acetonitrile (Salkowski, *B.* 17, 506).

p-**Amido-phenyl-acetic acid** $C_6H_4(NH_2).CH_2.CO_2H$ [1:4]. [200°]. From *p*-nitro-phenyl-acetic acid (Radziszewski, *B.* 2, 209; Bedson, *C. J.* 37, 92). White needles (from water); v. sl. sol. cold water.

Nitrile $C_6H_4(NH_2).CH_2.CN$. *p-Amido-benzyl cyanide.* [46°]. (312°). V.D. 4·78 (for 4·56). *Formation.*—1. From *p*-nitro-benzyl cyanide (Szumpelik, *B.* 3, 474; Gabriel, *B.* 15, 834).—2. As one of the products of the reduction of *α*-*p*-di-nitro-cinnamic ether (*q. v.*) by tin and HCl (Friedländer a. Mähly, *A.* 229, 229). The yield is 15 p.c. of the substance used. *Properties.*—Satiny plates (from water). Sol. acids. Gives a di-bromo-derivative. HCl at 130° converts it into amido-phenyl-acetic acid. Salts.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$. Acetyl derivative $NHAc.C_6H_4.CH_2.CN$. [97°]. Slender needles; v. sol. alcohol and ether. Di-acetyl derivative $NAc_2.C_6H_4.CH_2CN$. [153°]. Glistening needles. Sol. boiling water, benzene, and CS_2; sl. sol. alcohol.

Di-amido-phenyl-acetic acid $C_6H_3(NH_2)_2.CH_2CO_2H$ [4:3:1]. Formed by reducing (3, 4, 1)-nitro-amido-phenyl-acetic acid (Gabriel, *B.* 15, 1996). Short flat crystals (with aq). Sl. sol. hot alcohol, insol. ether, CS_2, chloroform, and benzene. Sol. acids and alkalis.

α-*m*-**Di-amido-phenyl-acetic acid** [1:3] $C_6H_4(NH_2).CH(NH_2).CO_2H$. [214°]. Formed by reducing *m*-nitro-phenyl-*α*-amido-acetic acid with tin and HCl (Plöchl a. Loë, *B.* 18, 1181). Flat silvery needles.

Salt.—CuA'_2: bluish-green crystalline pp.

o-**AMIDO-PHENYL-ACETYLENE** C_8H_7N *i.e.* $C_6H_4(NH_2).C{:}CH$. Yellowish oil. Prepared by reduction of *o*-nitro-phenyl-acetylene with zinc-dust and NH_3. It forms yellow pps. with ammoniacal $AgNO_3$ and Cu_2Cl_2.

B'HCl: soluble yellow crystals.

Reaction.—Converted by H_2SO_4 (12 pts.) and H_2O (4 pts.) into *o*-amido-acetophenone (Baeyer a. Bloem, *B.* 17, 964).

Acetyl derivative. [75°]. Colourless needles (Baeyer a. Landsberg, *B.* 15, 60).

Di-*o*-amido-di-phenyl-diacetylene $C_6H_4(NH_2).C{:}C.C{:}C.C_6H_4(NH_2)$. [128°]. Prepared by the action of a solution of potassium ferricyanide on the cuprous compound of *o*-amido-phenyl-acetylene. Long yellowish needles. Sol. alcohol, ether and acids, insol. water.

$B''H_2Cl_2$: colourless soluble crystals.

Di-acetyl derivative. [231°]. Long needles (Baeyer a. Landsberg, *B.* 15, 60).

(*B.* 2)-**AMIDO-**(*A*)-**PHENYL-ACRIDINE**

$$C_{19}H_{14}N_2 \textit{ i.e. } C_6H_4\left\langle\begin{array}{c}N\\ |\\ CPh\end{array}\right\rangle C_6H_3(NH_2).$$

Formed by heating phenyl-*p*-phenylene-diamine $C_6H_4(NH_2).NHC_6H_5$ with benzoic acid and $ZnCl_2$ (Hess a. Bernthsen, *B.* 18, 692). Amorphous solid. Easily soluble in ordinary solvents. The solutions of the base are yellow, the benzene and ethereal solution having a splendid green fluorescence. It dyes silk a brownish yellow. The solutions of its salts are red.

Di-amido-phenyl-acridine *v.* CHRYSANILINE.

AMIDO-PHENYL-ALANINE *v.* DI-AMIDO-PHENYL-PROPIONIC ACID.

AMIDO-PHENYL-AMIDO- *v.* DI-AMIDO-PHENYL- or PHENYL-DI-AMIDO-.

AMIDO-DI-PHENYL-AMINE $C_{12}H_{12}N_2$ *i.e.* $NH_2.C_6H_4.NH.C_6H_5$. [61°]. Prepared by the reduction of nitro-di-phenyl-amine or of phenyl-amido-benzene-azo-benzene, or its sulphonic acid (*Tropæolin* O O.) (Nietzki a. Witt, *B.* 12, 1399).

Thin laminæ. Gives quinone on oxidation.

Salt. $B'_2H_2SO_4$: silvery laminæ, sl. sol. water.

Acetyl derivative $C_{12}H_{11}AcN_2$. [158°].

p-*p*-**Di-amido-di-phenyl-amine** $NH_2.C_6H_4.NH.C_6H_4.NH_2$. [158°]. Formed by reduction of aniline black. Prepared by reducing (*α*)-di-nitro-di-phenyl-amine (N. a. W.).

Acetyl derivative. [239°].

Di-amido-di-phenyl-amine. Prepared by reducing (*β*)-di-nitro-di-phenyl-amine. Liquid.

Salts.—$B''H_2Cl_2$; sl. sol. water.—$B''H_2PtCl_6$.

Acetyl derivative. [203°].

Tri-amido-tri-phenyl-amine $(C_6H_4.NH_2)_3N$. [230°]. Formed by the reduction of tri-nitro-tri-phenyl-amine by $SnCl_2$ (Heydrick, *B.* 18, 2157; 19, 759.)

Salts.—$B'''3HCl$: needles. Its solution exhibits the following colour reactions: blue, turning violet with Fe_2Cl_6; bluish-green with ppd. MnO_2; blue with $K_2Cr_2O_7$; red with chloranil in acetic acid (but if in this case the free base is used the colour is bluish-green).—$B'''_23H_2PtCl_6$.—$B'''(C_6H_2(NO_2)_3OH)_3$.

Tri-acetyl derivative $N(C_6H_4.NHAc)_3$: needles which do not melt below 240°.

AMIDO-PHENYL-BENZGLYCOCYAMINE *v.* AMIDO-DI-PHENYL GUANIDINE CARBOXYLIC ACID.

p-**AMIDO-PHENYL-*iso*-BUTANE** $C_{10}H_{15}N$ *i.e.* $C_4H_9.C_6H_4.NH_2$. *Butyl-phenylamine. Amido-butyl-benzene.* (230°). S.G. $\frac{25}{}$ ·937. From aniline hydrochloride (10 g.) and iso-butyl alcohol (8 g.) by heating for 6 hours at 230° (A. Studer, *A.* 211, 237; *B.* 14, 1472, 2186; Pahl, *B.* 17, 1232). Colourless oil; v. sl. sol. water, volatile with steam. Miscible with alcohol or ether. Nitrous acid converts it into butyl-phenol.

Salts.—B'HCl.—B'HBr.—B'HI.

Acetyl derivative [170°]: laminæ.

Formyl derivative $C_{10}H_{13}.NH.CHO$ [59°]: laminæ (Gasiorowski a. Merz, *B.* 18, 1009).

AMIDO-PHENYL-BUTINENE $C_{10}H_{11}N$ probably $C_6H_4\overset{(3)}{(NH_2)}.\overset{(1)}{CH_2}.CH\left\langle\begin{array}{c}CH\\ \|\\ CH\end{array}\right.$. [98°]. (272° at 718 mm.). V.D. = 4·95 (for 5·02). Formed by reduction of *m*-nitro-*α*-methyl-cinnamic aldehyde in alcoholic solution with tin and HCl. Colourless glistening plates. Sublimes at 100°. Reduces ammoniacal $AgNO_3$. The

hydrochloride, sulphate and nitrate are easily soluble in water. The hydrochloride forms colourless glistening plates. $B'_2H_2Cl_2PtCl_4 2aq$: slender needles.

Acetyl derivative $C_{10}H_{10}NAc$ [140°]: colourless concentric prisms.

Benzylidene derivative $C_{10}H_9N{:}CHPh$ [73°]: concentric light-yellow needles. Formed by heating the base with benzaldehyde (Miller a. Kinkelin, *B.* 19, 1249).

o-AMIDO-PHENYL-CARBAMIC ETHER $C_9H_{12}N_2O_2$ *i.e.* $H_2N.C_6H_4.NH.CO_2Et$. *o-Amido-phenyl-urethane.* [86°]. Formed by reducing *o*-nitro-phenyl-carbamic ether (Rudolph, *B.* 12, 1295). Long colourless needles; sol. water.

Salt.—$B'HCl$: large tables.

p-Amido-phenyl-carbamic ether. *Amido-carbanilic acid.* [74°]. Formed by reducing *p*-nitro-phenyl-carbamic ether (Hager, *B.* 17, 2626; Behrend, *A.* 233, 10). Needles (from dilute alcohol); insol. water.

Salts.—$B'HCl$: long needles.—$B'H_2SO_4$.—$B'H_2C_2O_4$: needles, sol. hot water, sl. sol. cold water.—$B'_2H_2PtCl_6$: brown pp.—$(B'HCl)_3SnCl_4$. $B'_2SnCl_2 aq$.—$(B'HCl)_4HgCl_2$.

Benzoyl derivative $C_6H_4(NHBz).NH.CO_2Et$, [230°]: needles; sl. sol. alcohol, insol. water.

Di-*p*-amido-di-phenyl-carbamic ether $(C_6H_4.NH_2)_2N.CO_2Et$. *Di-p-amido-di-phenyl-amine urethane.* [101°]. Formed by reduction of di-*p*-nitro-di-phenyl-carbamic-ether. Violet needles (+aq). Soluble in water.

Di-benzoyl derivative $(C_6H_4.NHBz)_2N.CO_2Et$ [235°]: nearly colourless amorphous solid (Hager, *B.* 18, 2576).

DI-AMIDO-DI-PHENYL-CARBINOL $C_{13}H_{14}N_2O$ *i.e.* $C_6H_4(NH_2).CH(OH).C_6H_4NH_2$. (β)-*Di-amido-benzhydrol.* [128°–129°]. From (β)-di-amido-benzophenone [149°] and sodium amalgam (W. Staedel, *A.* 218, 350). Glittering plates. Salts.—$B''2HCl 2aq$.—$B''H_2SO_4 2aq$.

Acetyl-derivative. [220°].

Di-amido-tri-phenyl-carbinol $C_{19}H_{18}N_2O$ *i.e.* $C_6H_5C(OH)(C_6H_4NH_2)_2$ [below 100°].

Formation. — By the action of aniline in presence of H_2SO_4 upon the chloride $C_6H_5.CCl.C_6H_4.NH$.

Preparation.—From aniline hydrochloride (40 pts.), nitrobenzene (45 pts.), benzo-trichloride (40 pts.), and Fe at 180°. $C_6H_5CCl_3 + 2C_6H_5NH_2 = C_6H_5CCl(C_6H_4NH_2)_2 + 2HCl$. The mass is extracted with dilute HCl (which leaves some blue colouring matters undissolved) and the nitro-benzene is distilled off by steam (Doebner, *B.* 15, 234; *A.* 217, 242).

Properties. — Small crystals (from dilute alcohol). Insol. in cold water; v. sol. alcohol or benzene. On heating with MeI it gives malachite green.

Salts.—Dilute acids dissolve it in the cold, forming nearly colourless solutions which on boiling (split off water and) change to deep reddish-violet. The salts dye violet, but the shades are not fast. The coloured salts are probably of the form $C_6H_5C{<}^{C_6H_4NH_2}_{C_6H_4NH_2}$. This salt forms dark $\diagdown Cl$ blue needles with coppery lustre.

Reaction.—Zinc dust and HCl reduce it to di-amido-tri-phenyl-methane (*q. v.*).

Tri-amido-tri-phenyl-carbinols *v.* ROSANILINE.

DI-AMIDO-TRI-PHENYL-CARBINOL CARBOXYLIC ANHYDRIDE $C_{20}H_{16}N_2O_2$ *i.e.* $(C_6H_4NH_2)_2C.C_6H_4.CO.O$. [265°–266°]. Small colourless needles. Is prepared by heating phenolphthaleïn with aqueous NH_3. Gives a *tetra-bromo-derivative* [280°], and a *tetra-acetyl-tetra-bromo-derivative* [241°] (Baeyer a. Burkhardt, *B.* 11, 1297).

AMIDO-DIPHENYL CARBOXYLIC ACID *v.* AMIDO-DIPHENIC ACID.

DI-AMIDO-DI-PHENYLENE KETONE OXIDE (so called) $C_{13}H_{10}N_2O_2$ *i.e.* $C_{13}H_6(NH_2)_2O_2$. *Lactone of oxy-di-amido-diphenyl carboxylic acid.* From the nitro compound by Sn and HCl (A. G. Perkin, *C. J.* 43, 190). Orange needles (from xylene). Very slightly soluble in boiling water. Ruby prisms (from dilute alcohol).

Salts. — Forms two hydrochlorides. — $(B''HCl)_2PtCl_4$.—$B''(2HCl)PtCl_4$.

AMIDO-PHENYLENE OXIDE C_6H_5NO *i.e.* $C_6H_3(NH_2)O$ (?). *Di-amido-di-phenylene di-oxide.* From nitro-phenylene oxide by alcoholic ammonium sulphide (Märker, *A.* 124, 251). Yellow needles, sl. sol. water, v. sol. hot alcohol.—$B'_2H_2PtCl_6$.

DI-AMIDO-DIPHENYLENE-QUINOXALINE

$C_6H_2(NH_2)_2{<}^{N.C.C_6H_4}_{N.C.C_6H_4}$. Formed by the action of phenanthraquinone upon tetra-amido-benzene [1:2:4:5]. Orange-yellow needles. Nearly insol. acetic acid. Weak base. Dissolves in conc. H_2SO_4 with a greenish-blue colour, passing through violet into red on dilution (Nietzki a. Hagenbach, *B.* 20, 338).

AMIDO-PHENYLENE-UREA $C_7H_7N_3O$ *i.e.* $OC{<}^{NH}_{NH}{>}C_6H_3(NH_2)$ [1:2:4]. Formed by reducing di-nitro-phenyl-urethane with tin and HCl (Hager, *B.* 17, 2631).

Salts. — $B''H_2SnCl_4$: long needles. — $B''C_6H_2(NO_2)_3OH$: greenish-yellow needles.

o-AMIDO-PHENYL-ETHANE $C_8H_{11}N$ *i.e.* $C_6H_4(NH_2).CH_2.CH_3$ [1:2]. *o-Ethyl-phenyl-amine. o-Amido-ethyl-benzene.* (211°). S.G. $\frac{22}{}$ ·983. From *o*-nitro-phenyl-ethane, tin, and HCl (Beilstein a. Kuhlberg, *A.* 156, 206). Liquid at −10°. Salt.—$B'HNO_3$.

Acetyl derivative $C_8H_{10}AcN$. [112°]. (305°).

Benzoyl derivative $C_8H_{10}BzN$. [147°]: small glittering plates (Paucksch, *B.* 17, 2800).

o-Amido-phenyl-ethane sulphonic acid $C_6H_3Et(NH_2).SO_3H$. Formed by sulphonation of the acetyl derivative. White needles (P.).

p-Amido-phenyl-ethane $C_6H_4(NH_2).CH_2.CH_3$ [1:4]. *p-Ethyl-phenyl-amine.* '*Phenethylamine.*' [−5°]. (214°). S.G. $\frac{22}{}$ ·975. From *p*-nitro-phenyl-ethane by reduction (B. a. K.) or from aniline by heating with ethyl alcohol and $ZnCl_2$ (Benz, *B.* 15, 1647). Formed also when ethyl-aniline hydrochloride is heated at 300° (Hofmann, *B.* 7, 526). Colourless oil; volatile with steam. Salts.—*$B'HNO_3$: small needles or prisms, sl. sol. cold, v. sol. hot, water.—$B'_2H_2SO_4$: large white plates, sl. sol. cold water, m. sol. dilute H_2SO_4.—$B'HCl$.—$B'_2H_2PtCl_6$.

Acetyl derivative $C_6H_4(NHAc).C_2H_5$ [95°]. (316°).

Benzoyl derivative $C_6H_4(NHBz)C_2H_5$. [151°]: long needles (P.).

ω-Amido-phenyl-ethane $C_6H_5.CH_2.CH_2.NH_2$. [198°]. *Phenylethyl-amine.*

Formation.—1. By dry distillation of α-amido-phenyl-propionic acid (*q.v.*) (Schulze a. Barbieri, *J. pr.* [2] 27, 346; Erlenmeyer a. Lipp, *A.* 219, 202).—2. By action of zinc and HCl upon the cyanhydrin of benzoic aldehyde, or upon amygdalin (Fileti, *B.* 12, 297, 1700).—3. By action of bromine on an alkaline solution of phenyl-propionamide (Hofmann, *B.* 18 2740).

Preparation. — By reducing an alcoholic solution of benzyl cyanide with zinc and HCl (Bernthsen, *A.* 184, 290), di-phenylethyl-amine $(C_6H_5.CH_2.CH_2)_2NH$, and tri-phenylethyl-amine $(C_6H_5CH_2CH_2)_3N$, being also formed (Spica, *G.* 1875, 124; 1879, 566).

Properties.—Liquid; sl. sol. water. Absorbs CO_2 from the air, being converted into a solid carbonate [105°], out of which, on heating, another carbonate, [88°], sublimes. Oxidised to benzoic acid by chromic mixture.

Salts.—B'HCl, [217°]: trimetric tablets (from cold alcohol) or satiny plates (from alcohol-ether): v. sol. alcohol or water, insol. ether.—$B'_2H_2PtCl_6$; more soluble in hot water than in hot alcohol.

Di-amido-di-phenyl-ethane *v.* Di-amido-di-benzyl.

ω-AMIDO-TRI-PHENYL-ETHANE $C_{20}H_{19}N$ *i.e.* $CPh_3.CH_2.NH_2$. [116°]. From tri-phenyl-aceto-nitrile by reduction with zinc and HCl. Crystals; v. sol. ether, sl. sol. cold alcohol. The hydrochloride forms needles, [247°], v. sl. sol. water, v. sol. alcohol (Elbs, *B.* 17, 700).

AMIDO-PHENYL-ETHYLENE *v.* Amido-styrene.

Di-*p*-amido-di-phenyl-ethylene $C_{14}H_{14}N_2$ *i.e.* $C_2H_2(C_6H_4.NH_2)_2$. *Di-amido-stilbene.* [227°].

Formation.—1. By reduction of di-*p*-nitro-di-phenyl-ethylene with tin and HCl.—2. By reduction with $SnCl_2$ of the brownish-red product of condensation (azoxy-di-phenyl-ethylene?) obtained by the action of sodium methylate or alcoholic NaOH upon *p*-nitro-toluene.

Reactions.—By *nitrous acid* it is converted into a tetrazo-compound which by combination with the sulphonic acids of amines and phenols yields a series of colouring-matters which dye cotton from a soap bath. Thus (α)-naphthol-sulphonic acid gives a bluish-violet, (β)-naphthol-(R)-di-sulphonic acid a blue, (α)-naphthylamine-sulphonic acid a red, and salicylic acid a yellow, colouring-matter.

Di-acetyl derivative $C_2H_2(C_6H_4.NHAc)_2$: [312°] (Bender a. Schultz, *B.* 19, 3234).

Di-*p*-amido-di-phenyl-ethylene-di-carboxylic anhydride $\begin{matrix} C_6H_4(NH_2).C.CO \\ \| \\ C_6H_4(NH_2).C.CO \end{matrix}\!\!>O$. [280°]. Formed by reduction of the nitro compound (Reimer, *B.* 14, 1802). Small plates. Insol. most solvents.

Di-*p*-amido-di-phenyl-ethylene-di-sulphonic acid $C_2H_2(C_6H_3(NH_2)SO_3H)_2$. *Di-amido-stilbene-di-sulphonic-acid.* Obtained by reduction with zinc-dust of the brown product (azoxy- or azo-di-phenyl-ethylene-di-sulphonic acid?) which is formed by boiling *p*-nitro-toluene-*o*-sulphonic acid $C_6H_3Me(NH_2)SO_3H$ [1:4:2:] with aqueous NaOH. Microscopic needles. Nearly insol. water. Its salts are easily soluble. By nitrous acid it is converted into a tetrazo-compound which by combination with amines or phenols gives colouring-matters which have the property of dyeing cotton from a soap bath (Bender a. Schultz, *B.* 19, 3234).

***o*-AMIDO-PHENYL-GLYOXYLIC ACID** *v.* Isatic acid.

***m*-Amido-phenyl-glyoxylic acid** $C_8H_7NO_3$ *i.e.* $C_6H_4(NH_2)CO.CO_2H$ [1:3]. Colourless prisms or needles. [270°-280° with decomposition]. Prepared by reduction of *m*-nitro-phenyl-glyoxylic acid with alkaline $FeSO_4$.

Salts.—A'Ag: sparingly soluble crystalline powder.—$C_8H_7NO_3.HCl$: soluble flat prisms (Claisen a. Thompson, *B.* 12, 1946).

***p*-AMIDO-*s*-DI-PHENYL-GUANIDINE *m*-CARBOXYLIC ACID** $C_{14}H_{14}N_4O_2$ *i.e.* [1:4] $NH_2.C_6H_4.NH.C(NH).NH.C_6H_4.CO_2H$. *Amido-phenyl-benzglycocyamine.* Prepared by heating cyano-carbimido-amido-benzoic acid (*v.* p. 157) with *p*-phenylene-diamine (Griess, *B.* 16, 338). Small prisms. Salt.—$B''H_2Cl_2$.

***p*-amido-*s*-di-phenyl-guanidine *o*-carboxylic acid.** *Anhydride* $H_2N.C_6H_4.NH.C\!\!<\!\!\begin{matrix} NH.C_6H_4 \\ N - CO \end{matrix}\!\!>$ *Amido-phenyl-benzglycocyamidine.* Formed by boiling di-cyano-amido-benzoyl (*v.* p. 155) with an aqueous solution of *p*-phenylene-diamine (Griess, *B.* 18, 2421). Very small white needles; v. sol. hot water, m. sol. alcohol.

AMIDO-PHENYL-HYDROXIDE *v.* Amido-phenol.

***m*-AMIDO-PHENYL-HYDRAZINE** $C_6H_9N_3$ *i.e.* $C_6H_4(NH_2).NH.NH_2$ Formed by saponification of the oxamic acid $C_6H_4(NH.C_2O_2.OH).NH.NH_2$ which is obtained by reduction of *m*-diazo-phenyl-oxamic acid $C_6H_4(NH.C_2O_2.OH).N_2Cl$ with $SnCl_2$ (Griess, *B.* 18, 964). V. sol. alcohol and ether, sl. sol. water. Very oxidisable.

Amido-phenyl-hydrazine sulphonic acid $C_6H_3(NH_2)(N_2H_3)(SO_3H)$ [3:1:6]. Formed by reduction of nitro-phenyl-hydrazine sulphonic acid with NH_4HS or $SnCl_2$ (Limpricht, *B.* 18, 2194). Very soluble in water. Salts:—A'H,HCl easily soluble fine white needles.—$A'HH_2SO_4$: microscopic needles.—$A'H,HNO_3$: prisms.

AMIDO-DI-PHENYL-KETONE *v.* Amido-benzophenone.

***o*-AMIDO-PHENYL-MERCAPTAN** C_6H_7NS *i.e.* $C_6H_4(NH_2)(SH)$. *Amido-phenyl-sulphydrate.* [26°]. (234°).

Formation.—1. By fusing benzenyl-amido-phenyl-mercaptan (*q.v.*) with potash (Hofmann, *B.* 12, 2363).—2. Anhydro-oxalyl-amido-phenyl-mercaptan (easily prepared from acetanilide and sulphur) is fused with potash (3 pts.). The yield is nearly theoretical (Hofmann, *B.* 13, 1230). Colourless needles, very easily oxidised. It forms products of condensation with acids, aldehydes, and nitriles; thus acetic acid, acetyl chloride, acetonitrile, and aldehyde each produce ethenyl-amido-phenyl mercaptan (*q.v.*) $C_6H_4\!\!<\!\!\begin{matrix} N \\ S \end{matrix}\!\!>\!C.CH_3$.

***p*-Amido-diphenyl-mercaptan** [1:4] $H_2N.C_6H_4.C_6H_4.SH$ [1:4]. Prepared by reducing *p*-nitro-diphenyl sulphochloride with tin and HCl (Gabriel a. Damberger, *B.* 13, 1410).

Salt.—B'HCl: small glittering prisms.

AMIDO-PHENYL-METHANE v. TOLUIDINE.

m-**Amido-di-phenyl-methane** $C_{13}H_{13}N$ *i.e.* $C_6H_5.CH_2.C_6H_4.NH_2$. [46°]. Formed by reducing *m*-nitro-di-phenyl-methane (Becker, *B.* 15, 2092).

Acetyl derivative. [91°]: pearly plates.

p-**Amido-di-phenyl-methane.** [35°]. Formed by reducing *p*-nitro-di-phenyl methane with tin and HCl (Basler, *B.* 16, 2718). The sulphate is sl. sol. cold water.

di-amido-di-phenyl-methane $C_{13}H_{10}(NH_2)_2$. [85°]. Formed by reducing (*a*)-di-nitro-di-phenyl-methane (Doer, *B.* 5, 795). Pearly plates; sl. sol. water (Praetorius, *A.* 194, 348). The sulphate is v. sl. sol. water.

Tetra-amido-di-phenyl-methane $C_{13}H_8(NH_2)_4$. [161°]. By reduction of the nitro compound [172°] (Staedel, *A.* 218, 341). White needles (from benzene). M. sol. water, sl. sol. benzene.

Acetyl derivative $C_{13}H_8(NHAc)_4$. Crystalline powder. V. sl. sol. water; m. sol. alcohol.

Amido-tri-phenyl-methane $C_{19}H_{17}N$ *i.e.* $CHPh_2.C_6H_4.NH_2$. [84°]. Prepared by heating aniline hydrochloride with di-phenyl-carbinol and $ZnCl_2$ at 180° (Fischer a. Roser, *B.* 13, 674; *A.* 206, 155). Prisms or plates. Is a weak base. The benzene compound $(C_{19}H_{17}NC_6H_6)$ forms long colourless needles. **Salts.**—$B'HCl$: needles, sl. sol. water.—$B'H_2PtCl_6$.

Di-amido-tri-phenyl-methane $C_{19}H_{18}N_2$ *i.e.* $C_6H_5.CH(C_6H_4NH_2)_2$. [139°].

Formation.—1. From benzylidene chloride, aniline, and zinc dust (Böttinger, *B.* 12, 976).—2. From di-amido-tri-phenyl-carbinol by reducing with zinc dust (Doebner, *A.* 217, 246; *B.* 15, 236).—3. By heating aniline hydrochloride with benzoic aldehyde and fuming HCl (Mazzara, *G.* 14, 510).

Preparation.—A mixture of benzaldehyde (10 pts.), aniline sulphate (28 pts.), $ZnCl_2$ (20 pts.) and a little water, is heated on a water bath for several hours, the fused mass is boiled with dilute H_2SO_4, diluted, filtered, and the base precipitated with NH_3; yield 80 p.c. of the theoretical (Fischer, *B.* 15, 676).

Properties.—Colourless crystals (from ether) [139°]. Prisms containing benzene of crystallisation (from benzene) [106°]; at 120° the benzene goes off. V. sl. sol. water, sol. alcohol or ether.

Additional References.—C. Böttinger, *B.* 11, 276, 840; 13, 958; O. Fischer, *A.* 206, 147, 153; *B.* 13, 665.

Tri-amido-tri-phenyl-methane $C_{19}H_{19}N_3$ *i.e.* $CH(C_6H_4.NH_2\,[1:4])_3$. *Para-leucaniline.* [148°].

Formation.—1. By reducing tri-nitro-tri-phenyl-methane with zinc dust and glacial acetic acid (O. a. E. Fischer, *A.* 194, 272).—2. By reducing para-rosaniline (Hofmann, *Pr.* 12, 9).—3. By reducing nitro-di-amido-tri-phenyl-methane, prepared from aniline hydrochloride, *p*-nitro-benzoic aldehyde and $ZnCl_2$ (Fischer a. Greiff, *B.* 13, 670; Fischer, *B.* 15, 678).

Properties.—Colourless plates. Readily converted by oxidation into para-ROSANILINE (*q.v.*).

Salts.—$B'''H_2Cl_2aq$: short prisms, sl. sol. alcohol, ether, and HClAq.—The **sulphate** forms needles, v. sol. water, sl. sol. alcohol, insol. ether.—The **oxalate** forms prisms, v. sol. water.—The **platinochloride** forms sparingly soluble short needles.

Tri-acetyl derivative [177°]. Thin tables; when oxidised by $K_2Cr_2O_7$ and acetic acid it gives tetra-acetyl-para-rosaniline.

Tri-benzoyl derivative [149°]. Colourless needles; sol. alcohol, v. sl. sol. water, ether, and benzene (Renouf, *B.* 16, 1301).

m-p-p-**Tri-amido-tri-phenyl-methane** [1:3] $H_2N.C_6H_4.CH(C_6H_4.NH_2[1:4])_2$. *Pseudo-leucaniline.* [150°]. Obtained by reducing *m*-nitro-di-*p*-amido-tri-phenyl-methane (Fischer, *B.* 13, 673). Colourless crystals; sol. alcohol, sl. sol. ether or benzoline. Crystallises with benzene in white needles of $C_{19}H_{19}N_3C_6H_6$ [145°]. Gives, on oxidation, a violet colouring-matter.

Salts.—$B_2'''3H_2PtCl_6$: yellow crystalline pp., v. sol. water, m. sol. alcohol.

o-p-p-**tri-amido-tri-phenyl-methane** [1:2] $H_2N.C_6H_4.CH(C_6H_4NH_2[1:4])_2$. [165°]. Formed by reduction of the *o*-nitro-di-*p*-amido-tri-phenyl-methane obtained by heating *o*-nitro-benzoic aldehyde with aniline sulphate and $ZnCl_2$. Small crystals. On oxidation it gives a brown colouring matter.

Salts.—$B'''H_3Cl_3$: colourless easily soluble needles. The **sulphate** forms small quadratic tables, v. sol. water, sl. sol. alcohol. The **oxalate** forms small soluble needles (Renouf, *B.* 16, 1304).

AMIDO-PHENYL METHYL KETONE v. AMIDO-ACETOPHENONE.

p-**AMIDO-DI-PHENYL-METHYL-PYRAZOL-CARBOXYLIC ACID** $C_{17}H_{15}N_3O_2$ *i.e.*

$$\begin{array}{l}\quad\;\; N\text{———————}NPh \\ \quad\;\; \| \qquad\qquad\quad | \\ C_6H_4(NH_2).C.C(CO_2H):CMe\end{array}$$

[251°]. Formed by reduction of *p*-nitro-di-phenyl-methyl-pyrazol-carboxylic acid with $SnCl_2$ (Knorr a. Jödicke, *B.* 18, 2259). Crystalline powder. Sol. alcohol, ether, acids, and alkalis, insol. water. It evolves CO_2 at its melting-point.

m-**AMIDO-(*Py*.3)-PHENYL-(*Py*.2)-METHYL QUINOLINE**

$$C_{16}H_{14}N_2 \text{ i.e. } C_6H_4\left\langle\begin{array}{l}CH:CMe \\ \qquad\;\; | \\ N : C.C_6H_4(NH_2)\end{array}\right.$$

[115]. Obtained by reduction of *m*-nitro-phenyl-methyl-quinoline with tin and HCl (Miller a. Kinkelin, *B.* 19, 533). Prisms. Very soluble in alcohol and benzene, tolerably in ether. Has no dyeing power, although it is isomeric with flavaniline. By further reduction with tin and HCl it yields a tetrahydride.

Salts.—The mono-acid salts are yellow, the di-acid colourless.—$B''H_2Cl_2\,2aq$: easily soluble glistening prisms. $B''H_2Cl_2PtCl_4\,2aq$: orange tables.—$B''H_2Cl_2PtCl_4$: concentric yellow plates.

m-**Amido-(*Py.* 3)-phenyl-(*Py.* 2)-methyl-tetrahydro-quinoline**

$$C_6H_4\left\langle\begin{array}{l}CH_2.CHMe \\ \qquad\quad | \\ NH.CH.C_6H_4(NH_2)\end{array}\right.$$

Formed by reduction of amido-phenyl-methyl-quinoline with tin and HCl.

Di-acetyl derivative $C_{16}H_{16}N_2Ac_2$. [178°]. Thin colourless prisms; sol. hot alcohol.

p-**Amido-(Py. 3)-phenyl-(Py. 1)-methyl-quinoline** v. FLAVANILINE.

AMIDO-PHENYL-HYDRO-QUINOLINE v. AMIDO-PHENYL-QUINOLINE.

p-**AMIDO-PHENYL-OCTANE** $C_{14}H_{23}N$ *i.e.* $H_2N.C_6H_4.C_8H_{17}$. *Capryl-phenyl-amine. Phen-capryl-amine.* (291° corr.). Formed by heating a mixture of aniline, capryl alcohol, and $ZnCl_2$ at 280°. Or by heating aniline hydrochloride and

capryl alcohol at 200°–290° (Beran, *B.* 18, 139). Fluid at −20°. Colourless oil.

Salts.—$B'_2H_2SO_4$: v. sol. hot water, v. sl. sol. cold.—$B'_2H_2C_2O_4$: small plates, v. sol. alcohol and hot water, sl. sol. cold water.

Benzoyl derivative $C_{14}H_{21}.NHBz$. [109°]. Slender felted needles, v. sol. alcohol and ether when hot, sl. sol. when cold.

o-**Amido-phenyl-octane.** From the nitro-compound (Ahrens, *B.* 19, 2725).—$B'_2H_2SnCl_6$.

p-**Amido-ω-phenyl-*n*-octane.** [19·5°]. (311° cor.). From *n*-octyl alcohol, aniline, and $ZnCl_2$ (B.).—B'HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Formyl derivative. [56°].

Acetyl derivative. [93°].

Benzoyl derivative. [117°].

AMIDO-OPIANIC ACID $C_{10}H_{11}NO_5$ *i.e.* $C_6H(OMe)_2(NH_2)(CHO)(CO_2H)$ [6:5:3:2:1]. *Di-methoxy-amido-aldehydo-benzoic acid.* From nitroso-opianic acid, $SnCl_2$, and HCl. Crystalline. **Salt.**—HA'HCl: needles, decomposed by water.

Reactions.—1. *Baryta-water* give a blue-violet colour.—2. Fe_2Cl_6 gives a green colour in solutions of NH_4A'.—3. Hot Ac_2O gives granules of $C_{24}H_{24}N_2O_{11}$ [233°] (Kleemann, *B.* 20, 876).

DI-AMIDO-DI-PHENYL OXIDE $C_{12}H_{12}N_2O$ *i.e.* $(C_6H_4.NH_2)_2O$. [185°]. From the nitro compound (Hoffmeister, *A.* 159, 208). The **sulphate** forms slender needles.

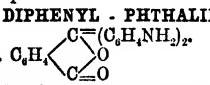
AMIDO-PHENYL-PENTANE *v.* AMIDO-AMYL-BENZENE.

TRI-AMIDO-TRI-PHENYL-PHOSPHINE OXIDE $C_{18}H_{18}N_3PO$ *i.e.* $OP(C_6H_4.NH_2)_3$. [259°]. Obtained by reduction of tri-nitro-tri-phenyl-phosphine-oxide (Michaelis a. Soden, *B.* 17, 923). White prisms. Soluble in hot water, hot alcohol, and acetone, sparingly in cold water, cold alcohol, and ether. Its salts are very soluble in water.

Tri-acetyl derivative $OP(C_6H_4.NHAc)_3aq.$ [188°], colourless crystals.

Tri-benzoyl derivative $OP(C_6H_4.NHBz)_3$ [c. 180°], crystalline powder.

DI-AMIDO-DIPHENYL-PHTHALIDE

$C_{20}H_{16}N_2O_2$ *i.e.* 

Lactone of di-amido-tri-phenyl-carbinol carboxylic acid. [180°]. Tables. Prepared by reduction of dinitro-diphenyl-phthalide. By the action of HNO_2 it gives phenol-phthaleïn (Baeyer, *B.* 12, 642; *A.* 202, 66).

AMIDO-PHENYL-PIPERIDINE $C_{11}H_{16}N_2$ *i.e.* $C_5NH_{10}.C_6H_4.NH_2$. [40°]. Formed by reduction of the corresponding nitro-compound [105°] with $SnCl_2$ and HCl.—$B''H_2Cl_2aq$: large colourless crystals (Lellmann, *B.* 20, 681).

p-**AMIDO-β-PHENYL-PROPANE** $C_9H_{13}N$ *i.e.* $H_2N.C_6H_4.CH_2.CH_2.CH_3$. *Amido-propyl-benzene. Propyl-phenyl-amine. Phenpropylamine.* (225°). From aniline, $ZnCl_2$, and propyl alcohol at 270° (Louis, *B.* 16, 105; Francksen, *B.* 17, 1220). Liquid, volatile with steam; v. sl. sol. water. **Salts**: B'HCl: laminæ, [204°].—$*B'_2H_2PtCl_6$.—B'HBr. [213°].—B'HI.—$B'_2H_2SO_4$: laminæ, sl. sol. cold water.—$B'_2H_2C_2O_4$: sl. sol. cold water.

Acetyl derivative $C_9H_{12}AcN$. [87°].

Benzoyl derivative $C_9H_{12}BzN$. [115°].

p-**Amido-α-phenyl-propane** $H_2N.C_6H_4.CH(CH_3).CH_3$. *Amido-isopropyl-benzene* (217°). Similarly prepared from isopropyl alcohol (L.). Liquid, sl. sol. water. **Salts**: $B'_2H_2SO_4$: sl. sol. cold water.—$B'_2H_2C_2O_4$.

Benzoyl derivative [115°]: laminæ.

See also CUMIDINE and PHENYL-PROPYL-AMINE.

o-**AMIDO-PHENYL-PROPIOLIC ACID** $C_9H_7NO_2$ *i.e.* $C_6H_4(NH_2).C{:}C.CO_2H$.

Preparation.—An ammoniacal solution of *o*-nitro-phenyl-propiolic acid is slowly added to a cold solution of $FeSO_4$ (11 pts.) saturated with NH_3; after 1 or 2 hours' standing the mixture is filtered and the amido-acid ppd. from the filtrate by adding HCl in slight excess; yield: 65 p.c. of the nitro-acid used (Richter, *B.* 16, 679).

Properties.—Microscopic needles. Soluble in alcohol, sparingly in ether, nearly insoluble in water, benzene, chloroform, and ligroine. Dissolves in aqueous acids. Decomposes on heating to about 125° and on boiling with water, in the latter case forming *o*-amido-acetophenone and CO_2. By boiling with NaOH and then adding HCl a splendid red colour is produced.

Salt.—$A'Ag^x$: insoluble pp.

Ethyl ether A'Et—[55°] needles (Baeyer a. Bloem, *B.* 15, 2147).

a-**AMIDO-*a*-PHENYL-PROPIONIC ACID** $C_9H_{11}NO_2$ *i.e.* $CH_3.C(C_6H_5)(NH_2).CO_2H$. *Amido-hydro-atropic acid.* From the nitrile by treatment with HCl (Tiemann a. Köhler, *B.* 14, 1981). Feather-like, satiny, needles. Sublimes about 260°. V. e. sol. water, insol. alcohol and ether. Converted by nitrous acid into atrolactic acid.

Nitrile $CH_3.CPh.(NH_2).CN$. Yellow oil.

β-**Amido-α-phenyl-propionic acid** $CH_2(NH_2).CH(C_6H_5).CO_2H$. [169·5°]. A product of action of conc. NH_3Aq on β-bromo-α-phenyl-propionic acid (Fittig a. Wurster, *A.* 195, 158; Merling, *A.* 209, 11). Plates (from water). Sl. sol. cold water.

o-**Amido-α-phenyl-propionic acid.** *Anhydride* or *lactam* $C_6H_4<\substack{NH \\ CHMe}>CO$. [119°]. *Atroxindol.* Formed, instead of the acid, by reducing $C_6H_4(NO_2).CHMe.CO_2H$. Needles (from dilute HCl). Sl. sol. cold water, forming a neutral solution; sol. alcohol and ether. When quite pure it has a pleasant smell. Slightly volatile with steam. It dissolves in alkalis but is reppd. by CO_2 (Trinius, *A.* 227, 274).

p-**Amido-α-phenyl-propionic acid** $CH_3.CH(C_6H_4NH_2).CO_2H$. [128°]. From nitro-hydro-atropic acid, Sn and HCl (Trinius, *A.* 227, 267). **Salt.**—HA'HCl; needles; v. sol. water.

α-**Amido-β-phenyl-propionic acid** $C_9H_{11}NO_2$ *i.e.* $C_6H_5.CH_2.CH(NH_2)CO_2H$.

Amido-hydro-cinnamic acid.

Occurrence.—In the radicles of germinating lupin seeds, together with other amido-acids. Forms about 1 p.c. of the dry seed. The mixture is heated with cupric hydrate and filtered, the acid is isolated from the residue by treatment with H_2S and subsequent evaporation (Schulze a. Barbieri, *J. pr.* [2] 27, 342; *B.* 14, 1785).

Formation.—From its nitrile by HCl (Erlenmeyer a. Lipp, *A.* 219, 194). The acid formed in this way is perhaps not identical with that in lupin seeds. An amido-phenyl-propionic acid identical with that in lupin seeds occurs among the products of the decomposition of proteïds by HCl. It melts at [275°–280°] and is optically active, while the acid from phenyl-acetic alde-

hyde melts at [263°-265°] and is inactive (Schulze a. Nägeli, *H.* 11, 201).

Properties.—Glittering, anhydrous, plates (from hot saturated solutions); groups of slender needles, containing aq (from dilute solutions) (S. a. B.). Satiny plates (from alcohol); short anhydrous prisms or stars (from water) (E. a. L.). Sweet taste. Neutral reaction. M. sol. water, v. sl. sol. alcohol, insol. ether. Small quantities may be sublimed. Gives no colour with Millon's reagent.

S a l t s.—CuA'_2: insol. water (S. a. B.).—$CuA'_2 2aq$: rosettes of small blue prisms (E. a. L.).—AgA'.—$HA'HCl$: prisms or stars; v. sol. alcohol or water, insol. conc. HCl.—$(HA'HCl)_2PtCl_4$.—$HA'HNO_3$.—$(HA')_2H_2SO_4$.

Reactions.—1. With $K_2Cr_2O_7$ and H_2SO_4 gives off odour of benzoic aldehyde, and ultimately forms benzoic acid.—2. When heated it cakes together and at about 270° it melts giving off CO_2, H_2O, and exo-amido-phenyl-ethane (*q. v.*); the residue may be crystallised from alcohol, it melts at [280°] and has the formula C_8H_9NO. From the behaviour of the analogous amido-propionic acid, we may suppose this body to be phenyl-lactimide.—3. By putrefaction it gives phenyl acetic acid.

N i t r i l e $C_6H_5.CH_2.CH(NH_2).CN$. From the compound of HCN with phenyl-acetic aldehyde by heating with alcoholic NH_3 at 100° (Erlenmeyer a. Lipp, *A.* 219, 189). Small crystals.

S a l t s.—$B'HCl$: trimetric prisms; v. sol. alcohol, insol. ether, v. e. sol. water.

A n h y d r i d e or *l a c t a m* C_9H_9NO or $C_{18}H_{18}N_2O_2$ *i.e.* $Ph.CH_2.CH<\begin{matrix}NH\\CO\end{matrix}>$ or

$Ph.CH_2.CH<\begin{matrix}NH.CO\\CO.NH\end{matrix}>CH.CH_2Ph$.

Phenyl-lactimide. [291°]. A by-product in the conversion of the acid into amido-phenyl-ethane by the action of heat. Very slender silky needles (from alcohol) forming an electric powder. May be sublimed as woolly needles. V. sl. sol. water, HCl, or KOHAq; insol. ether; sl. sol. glacial acetic acid.

β-Amido-β-phenyl-propionic acid $C_6H_5.CH(NH_2).CH_2.CO_2H$.

β-Amido-hydro-cinnamic acid. [121°]. From β-bromo-β-phenyl-propionic acid and conc. aqueous NH_3 at 0° (Posen, *A.* 195, 144; 200, 97). Large monoclinic crystals (from water); m. sol. cold water, v. sol. alcohol, v. sl. sol. ether. Boiling HClAq splits it up into NH_3 and cinnamic acid. S a l t.—$B'HCl$; prisms, v. sol. water.

A n h y d r i d e or *l a c t a m*

$C_6H_5.CH<\begin{matrix}CH_2\\NH\end{matrix}>CO$. *Phenyl-lactimide.* [147°].

Formed, instead of a sulphate, when the acid is added to H_2SO_4 (1 vol.) diluted with water (1 vol.). Needles, insol. cold water, m. sol. hot water, alcohol, or ether. Is not reconverted into the amido acid by prolonged boiling with water.

o-Amido-β-phenyl-propionic acid

A n h y d r i d e or *l a c t a m* C_9H_9NO ***i.e.***

$C_6H_4<\begin{matrix}NH.CO\\CH_2.CH_2\end{matrix}>$ or $C_6H_4<\begin{matrix}N:C(OH)\\CH_2.CH_2\end{matrix}>$.

Hydro-carbostyril. Di-hydro-(Py. 3)-oxy-quinoline. [160°]. Formed, instead of the amido acid, when o-nitro-β-phenyl-propionic acid is reduced by tin and HCl (Glaser a. Buchanan, *Z.* 1869, 194). Prisms; v. sl. sol. water v. sol. alcohol, ether, and warm conc. HClAq. May be distilled. PCl_5 at 140° converts it into di-chloro-quinoline.

E t h y l d e r i v a t i v e $C_9H_8N(OEt)$. [199°]. Formed by reducing the ethyl derivative of carbostyril with sodium amalgam (Friedländer a. Ostermayer, *B.* 15, 335). Silvery plates.

***m*-Amido-β-phenyl-propionic acid** $C_6H_4(NH_2).CH_2.CH_2.CO_2H$. *m-Amido-hydro-cinnamic acid.* [85°]. Formed by reduction of *m*-nitro-β-phenyl-propionic acid with tin and HCl (Gabriel, *B.* 15, 846). Colourless crystals. V. sol. water, alcohol, and ether. S a l t.—$A'HHCl$: colourless needles or scales.

***p*-Amido-β-phenyl-propionic acid** $C_6H_4(NH_2).CH_2.CH_2.CO_2H$. *p-Amido-hydro-cinnamic acid.* [131°] (Glaser a. Buchanan, *Z.* 1869, 195). Prepared by reduction of *p*-nitro-phenyl-propionic acid with $FeSO_4$ and NH_3. S a l t s.—$B'HCl$.—$B'_2H_2SO_4$.

A c e t y l d e r i v a t i v e $C_6H_4(NHAc)C_2H_4.CO_2H$. [143°]. Long colourless needles or short prisms. Sol. alcohol and ether, insol. CS_2 (Gabriel, *B.* 15, 843).

α-β-di-amido-β-phenyl-propionic acid.

A n h y d r i d e or *l a c t a m*

$C_6H_5.CH.CH(NH_2).CO$
NH ———

α-B e n z o y l d e r i v a t i v e

$C_6H_5.CH.CH(NHBz).CO$
NH ——— . [187°]. Formed by heating benzoyl-imido-cinnamic acid,

$C_6H_5.CH.CH.CO_2H$
NBz , with strong aqueous NH_3.

Glistening needles or prisms; sol. hot alcohol and acetic acid, sl. sol. ether, insol. water, dilute acids and alkalis. By boiling with HCl it loses NH_3 giving the benzoyl derivative of α-amido-cinnamic acid (Plöchl, *B.* 17, 1616).

α-p-di-amido-β-phenyl-propionic acid $C_9H_{12}N_2O_2aq$ *i.e.* $C_6H_4(NH_2)CH_2.CH(NH_2)CO_2Haq$ [245°-250°]. *p-Amido-phenyl-alanine.* Got by reducing *p*-nitro-α-amido-phenyl-propionic acid (Erlenmeyer a. Lipp, *A.* 219, 219), or by reducing α-*p*-di-nitro-cinnamic ether and saponifying the product (Friedländer a. Mähly, *B.* 16, 852; *A.* 229, 226). Silky needles (from water), sl. sol. alcohol, insol. ether. Neutral; has a sweet taste. Reduces salts of gold and silver. Does not give Hoffmann's mercury reaction (*A.* 87, 124). Gives off no NH_3 when boiled with KOH. Converted by nitrous acid into tyrosine.

S a l t s.—$HA'2HCl$.—$HA'H_2PtCl_6$.—CuA'_2; small violet-blue crystals, sl. sol. water.—$HA'H_2SO_4$: small needles.

(4,2,1)-di-amido-β-phenyl-propionic acid (4:2:1), $C_6H_3(NH_2)_2.CH_2.CH_2.CO_2H$.

A n h y d r i d e or *l a c t a m* $C_9H_{10}N_2O$ ***i.e.*** $H_2N.C_6H_3<\begin{matrix}CH_2.CH_2\\NH.CO\end{matrix}>$. *Amido-hydro-carbostyril.* (*Py.* 3)-*oxy*-(*B.* 3)-*amido-di-hydro-quinoline.* [211°]. Formed by reducing (4,2,1)-di-nitro-β-phenyl-propionic acid (Gabriel a. Zimmermann, *B.* 12, 602). Needles or prisms. Not affected by boiling alkalis. S a l t.—$B'HCl$.

(4:3:1)-Di-amido-β-phenyl-propionic acid. [4:3:1] $C_6H_3(NH_2)_2.CH_2.CH_2.CO_2H$. *Di-amido-hydro-cinnamic acid.* [144°, dry]. Formed by reduction of *m*-nitro-*p*-amido-phenyl-propionic

acid with tin and HCl (Gabriel, *B.* 15, 2291). Thick crystals containing aq. Sol. alcohol and acetic acid, v. sl. sol. ether, chloroform, benzene, and CS_2. Dissolves in aqueous acids and alkalis.

***m*-AMIDO-(*Py.* 3)-PHENYL-QUINOLINE**

$C_{15}H_{12}N_2$ *i.e.* $C_6H_4\left\langle\begin{array}{l}CH:CH\\ \quad\;\; \vert \\ N:C.C_6H_4(NH_2)\end{array}\right.$ [120°].

Formed by reduction of *m*-nitro-phenyl-quinoline with tin and HCl (Miller a. Kinkelin, *B.* 18, 1904). Long glistening needles. Distils at a high temperature undecomposed. Sol. ether, benzene, and hot water, v. sl. sol. cold water.

Salts.—$B''H_2Cl_2$: easily soluble colourless needles.—$B''H_2Cl_2PtCl_4$: yellow crystalline powder. — $B''_2H_2Cl_2PtCl_4$: long fine needles. — $B''H_2SO_4$2aq: thick colourless prisms.

(α)-Amido-(*Py.* 1)-phenyl-quinoline

$C_{15}H_{12}N_2$ *i.e.* $C_6H_4\left\langle\begin{array}{l}C(C_6H_4.NH_2):CH\\ \qquad\qquad\quad \vert \\ N=\!=\!=\!=\!=\!=CH\end{array}\right.$ [150°].

Obtained by reduction of the corresponding nitro-compound [187°] with $SnCl_2$. Colourless glistening plates (from alcohol). V. e. sol. alcohol, benzene, and chloroform, v. sl. sol. ether with a bluish-violet fluorescence. Volatilises undecomposed. Its mono-acid salts have a deep yellow colour and dye wool yellow, the di-acid salts are colourless.—×$B''HI$: soluble yellow needles.—×$B''_2H_2Cl_2PtCl_4$: yellow prismatic needles. The chromate is a sparingly soluble brown pp. (Kœnigs a. Nef, *B.* 20, 627).

(β)-Amido-(*Py.* 1)-phenyl-quinoline

$C_{15}H_{12}N_2$ *i.e.* $C_6H_4\left\langle\begin{array}{l}C(C_6H_4.NH_2):CH\\ \qquad\qquad\quad \vert \\ N=\!=\!=\!=\!=\!=CH\end{array}\right.$ [198°].

Obtained by reduction of the corresponding nitro-compound [118°] with $SnCl_2$. Four-sided prisms. Sl. sol. alcohol and benzene, v. sol. chloroform, v. sl. sol. ether. The ethereal solution has a bluish-violet fluorescence. It volatilises undecomposed. Its mono-acid salts have a yellow colour and dye wool yellow, the di-acid salts are colourless.—×$B''H_2Cl_2PtCl_4$: yellow prisms, sol. HCl, nearly insol. water (Kœnigs a. Nef, *B.* 20, 628).

Amido-phenyl-quinoline. [136·5°]. V.D. 7·67 (for 7·62). Obtained by heating quinoline hydrochloride with aniline (Jellinek, *M.* 7, 351). Yellowish white needles; insol. cold water, sol. benzene, alcohol, and chloroform.

Salts.—B''2HCl.—$B''H_2PtCl_6$.

Methylo-iodide. $B''MeI$. [220°].

***m*-Amido-(*Py.* 3)-phenyl-hydroquinoline**

$C_6H_4\left\langle\begin{array}{l}CH_2.CH_2\\ \quad \vert \\ NH.CH.C_6H_4(NH_2)\end{array}\right.$ Thick syrup.

Formed by reduction of *m*-amido-phenyl-quinoline or of *m*-nitro-phenyl-hydroquinoline with tin and HCl (Miller a. Kinkelin, *B.* 18, 1907).—$B''H_2Cl_2$: monoclinic tables.

(*Py.* 1:2)-AMIDO-PHENYL-ISOQUINOLINE

$C_{15}H_{12}N_2$ *i.e.* $C_6H_4\left\langle\begin{array}{l}C(NH_2):CPh\\ \qquad\quad\; / \\ CH:N\end{array}\right.$ [c. 100°].

Formed by reduction of (*Py.* 4:1:2)-chloro-nitro-phenyl-isoquinoline by heating with HI and P (Gabriel, *B.* 19, 834). Yellowish plates or needles. Easily soluble in ordinary solvents, moderately in ether and ligroine. Dissolves readily in acids. Salts.—$B'HI$: yellow crystals.—$B'_2H_2Cl_2PtCl_4$: long orange-red needles. —$B'HCl$×: flat needles.

DI-AMIDO-DI-PHENYL SULPHIDE

$C_{12}H_{12}N_2S$ *i.e.* $(C_6H_4NH_2)_2S$. *Thioaniline.* [105°]. Mol. w. 216. Obtained by heating aniline (6 pts.) with sulphur (1 pt.) at 160°, with gradual addition of PbO (Merz a. Weith, *B.* 4, 384); or from di-phenyl sulphide by nitration and reduction (Krafft, *B.* 7, 384). A small quantity is got by the action of S_2Cl_2 on aniline (Schmidt, *B.* 11, 1168). Long thin needles (from water). V. sl. sol. cold water, sl. sol. hot water, v. sol. alcohol, ether, and hot benzene. Not attacked by hot conc. HCl, by hot alcoholic KOH, or by sodium-amalgam. Its solutions give a blue colour when warmed with Fe_2Cl_6. Conc. H_2SO_4 dissolves it with violet colour.

Salts.—$B''H_2Cl_2$2aq: prisms, v. sol. water, sl. sol. alcohol or cold conc. HCl.—B''HCl2aq.—$B''H_2PtCl_6$. — $B''H_2SO_4$aq. — $B''_2H_2SO_4$aq. — $B''H_2C_2O_4$.

Diacetyl derivative $(C_6H_4NAcH)_2S$. [215°]. Needles.

Di-*o*-amido-di-phenyl di-sulphide $C_{12}H_{12}N_2S_2$ *i.e.* $(C_6H_4NH_2)_2S_2$. [93°]. Prepared by oxidising *o*-amido-phenyl mercaptan with Fe_2Cl_6 (Hofmann, *B.* 12, 2363). Plates; insol. water, sol. alcohol. Readily reduced back to the mercaptan. The hydrochloride forms laminæ, sl. sol. HClAq.

Di-*p*-amido-di-phenyl di-sulphide $(C_6H_4NH_2)_2S_2$. [79°]. Formed by saponifying its acetyl derivative with dilute H_2SO_4. Long greenish needles (from water); v. sl. sol. water, v. sol. alcohol.

Salts.—$B''H_2SO_4$2aq: small needles.

Di-acetyl derivative $(C_6H_4NAcH)_2S_2$. [c. 217°]. Formed, together with the diacetyl derivative of di-amido-di-phenyl tri-sulphide, by heating acetanilide with S_2Cl_2 at 100° (Schmidt, *B.* 11, 1171).

Di-amido-di-phenyl tri-sulphide. *Di-acetyl derivative* $(C_6H_4NAcH)_2S_3$. [214°]. Prepared as described above; forms laminæ (from glacial acetic acid).

AMIDO-DI-PHENYL SULPHONE

$C_{12}H_{11}NSO_2$ *i.e.* $C_6H_5.SO_2.C_6H_4.NH_2$. *Amido-sulphobenzide.* From nitro-di-phenyl sulphone by alcoholic ammonium sulphide (Gericke, *A.* 100, 209). Minute prisms, sl. sol. cold water.

Salts.—$B'HCl$: [c. 90]; reddish four-sided prisms.—$B'_2H_2PtCl_6$.

Di-amido-di-phenyl sulphone $C_{12}H_{12}N_2SO_2$ *i.e.* $(C_6H_4NH_2)_2SO_2$. [168°] (Schmid a. Nölting, *B.* 9, 80). Obtained in the same way from di-nitro-di-phenyl sulphone. Four-sided prisms, sl. sol. cold water.

Salts.—$B''H_2Cl_2$: long prisms.—$B''H_2PtCl_6$.

Di-amido-di-phenyl-sulphone di-carboxylic acid $C_{14}H_{12}N_2SO_6$ *i.e.* $SO_2(C_6H_3(NH_2)CO_2H)_2$, [above 350°]. Obtained from *p*-amido-benzoic acid and fuming H_2SO_4 at 180° (Michael a. Norton, *B.* 10, 580). Rose-red tufts of crystals (from water), sl. sol. alcohol.

Salt.—Ag_2A'': small white laminæ.

AMIDO-DI-PHENYL SULPHONIC ACIDS *v.* AMIDO-DIPHENYL.

AMIDO-PHENYL SULPHYDRATE *v.* AMIDO-PHENYL MERCAPTAN.

AMIDO-DIPHENYL DI-SULPHYDRATE $C_{12}H_{11}NS_2$ *i.e.* $C_{12}H_7(NH_2)(SH)_2$. [153°]. Prepared by reducing nitro-diphenyl di-sulphochloride with tin and HCl (Gabriel a. Dambergis, *B.* 13, 1411). Long needles.

***p*-AMIDO-DIPHENYL-*p*-THIO-GLYCOLLIC ACID** $C_{14}H_{13}NSO_2$ *i.e.* $H_2N.C_6H_4.C_6H_4.S.CH_2.CO_2H$. [Over 200°]. Formed by action of a chloro-acetate upon *p*-amido-diphenyl *p*-sulphydrate (Gabriel a. Dambergis, *B.* 13, 1410). Plates; sl. sol. water.

***o*-AMIDO-*s*-DI-PHENYL-THIO-UREA** $C_{13}H_{13}N_3S$ *i.e.* $C_6H_5NH.CS.NH.C_6H_4.NH_2$. From *o*-phenylene-diamine and phenyl thio-carbimide in benzene (Lellmann a. Würthner, *A.* 228, 212). Glittering prisms, v. sol. alcohol and glacial acetic acid, sl. sol. benzene, insol. ether. In a capillary tube it cakes together at 141°; at 185° aniline distils out of it; but at 250° it is still solid: *o*-phenylene-thio-urea being left: $PhHN.CS.NH.C_6H_4NH_2 =$

$$CS\Big\langle\begin{matrix}NH\\NH\end{matrix}\Big\rangle C_6H_4 + PhNH_2.$$

***m*-Amido-di-phenyl-thio-urea.** [148°]. From *m*-phenylene-diamine and phenyl thio-carbimide in benzene (L. a. W.). Amorphous yellow powder or colourless prisms (from alcohol). V. sol. glacial acetic acid, m. sol. alcohol, insol. ether and benzene. May be melted without decomposition. Decomposed by long boiling with alcohol, as follows: $2CS(NPhH)(NH.C_6H_4NH_2) = (PhHN.CS.NH)_2C_6H_4 + C_6H_4(NH_2)_2$. The *o* and *p* isomerides behave similarly.

***p*-Amido-*s*-di-phenyl-thio-urea.** From *p*-phenylene diamine and PhNCS dissolved in benzene (L. a. W.). Reddish prisms (from alcohol). Sol. glacial acetic acid, insol. ether or benzene. Begins to decompose at 163°, forming *p*-phenylene-thio-urea and aniline.

AMIDO-*p*-PHENYL-TOLUENE $C_{13}H_{13}N$ *i.e.* $C_{13}H_{11}.NH_2$. [93°-97°]. *Amido-tolyl-phenyl.* Obtained from *p*-phenyl-toluene, $C_6H_5.C_6H_4.CH_3$, by nitration and reduction (Carnelley, *C. J.* 29, 21).

Salt.—B'HCl. [c. 283°].

DI AMIDO-PHENYL-TOLYL-KETONE $C_{14}H_{14}N_2O$ *i.e.* $H_2N.C_6H_4.CO.C_6H_3(CH_3).NH_2$. [about 220°]. Colourless needles. Formed together with oxy-amido-phenyl-tolyl-ketone and di-oxy-benzophenone by heating commercial rosaniline with water at 270°.

Di-benzoyl derivative $C_{14}H_{10}O(NHBz)_2$. [226°], colourless needles (Liebermann, *B.* 16, 1927).

DI-AMIDO-PHENYL-TOLYL-METHANE *v.* DI-AMIDO-BENZYL-TOLUENE.

Di-amido-phenyl-di-tolyl-methane $C_{21}H_{22}N_2$ *i.e.* $C_6H_5CH(C_7H_6NH_2)_2$. [185°]. Formed by heating a mixture of *p*-toluidine, *p*-toluidine hydrochloride, and benzoic aldehyde for several hours at 120° (Ullmann, *B.* 18, 2094). It forms a compound with benzene, crystallising in glistening needles.

Tri-amido-di-phenyl-tolyl-methane $C_{20}H_{21}N_3$ *i.e.* $(H_2N.C_6H_4)_2CH.C_7H_6.NH_2$. *Leucaniline.* [100°]. Obtained by reducing rosaniline (*q. v.*) (Hofmann, *Pr.* 12, 9; Rosenstiehl a. Gerber, *A. Ch.* [6] 2, 341). Small crystals (from boiling water). Sl. sol. hot water, or ether, v. sol. alcohol. Converted into rosaniline by oxidation. Salts.—$B'''H_3Cl_3$ aq.—$B'''_23H_2PtCl_6$.—$B'''3HNO_3$.

Tri-acetyl derivative [168°]. Needles. Gives tetra-acetyl-rosaniline when oxidised with $K_2Cr_2O_7$ and acetic acid (Renouf, *B.* 16, 1303).

Tri-*p*-amido-phenyl-di-tolyl-methane $C_{21}H_{23}N_3$ *i.e.* $(H_2N.C_7H_6)_2CH.C_6H_4.NH_2$. Prepared by reduction of nitro-di-amido-phenyl-di-tolyl-methane with zinc dust and HCl (Fischer, *B.* 15, 680). Small colourless prisms or long needles. On oxidation it gives a rosaniline which dyes a bluer shade than ordinary rosaniline.

***o*-AMIDO-*s*-DI-PHENYL-UREA** $C_{13}H_{13}N_3O$ *i.e.* $NH_2.C_6H_4.NH.CO.NHC_6H_5$. From phenyl cyanate and *o*-phenylene diamine in benzene solution (Lellmann a. Würthner, *A.* 228, 220). Slender silky needles (from alcohol). V. sol. glacial acetic acid, m. sol. alcohol, v. sl. sol. benzene, insol. ether. In capillary tubes it cakes together and partially melts at 182°, splitting up into aniline and phenylene-urea, [305°].

***m*-Amido-*s*-di-phenyl-urea.** From *m*-phenylene diamine and PhNCO in benzene (L. a. W.). Grey needles (from dilute alcohol). V. sol. alcohol, and glacial acetic acid, sl. sol. ether and benzene. In capillary tubes it decomposes at 185° into aniline and *m*-phenylene-urea, [above 300°].

***p*-Amido-*s*-di-phenyl-urea.** From *p*-phenylene-diamine and PhNCO in benzene (L. a. W.). Slender white needles (from alcohol). Sol. glacial acetic acid, v. sl. sol. benzene, insol. ether. Decomposes about 210°-220° into aniline and *p*-phenylene-urea [above 320°].

Di-amido-di-phenyl-urea $C_{13}H_{14}N_4O$ *i.e.* $CO(NH.C_6H_4.NH_2)_2$. From tetra-nitro-di-phenyl-urea, $(C_6H_3(NO_2)_2.NH)_2CO$ by reducing with tin and HCl (Fleischer a. Nemes, *B.* 10, 1296). Laminæ (from alcohol); sl. sol. cold water.—$B'_2H_2PtCl_6$.

AMIDO-PHENYL-URETHANE *v.* AMIDO-PHENYL-CARBAMIC ETHER.

***o*-AMIDO-PHENYL-VALERIC ACID** [1:2] $C_6H_4(NH_2).CH_2.CH_2.CH_2.CH_2.CO_2H$. [62°]. White needles. Formed by boiling an alcoholic solution of *eso*-di-bromo-amido-phenyl-valeric acid with sodium-amalgam. It could not be converted into an inner-anhydride even by dehydrating-agents. *Acetyl derivative*: [151°] (Diehl a. Einhorn, *B.* 20, 385).

AMIDO-PHOSPHENYLIC ACID *v.* PHOSPHINES.

AMIDO-PHTHALIC ACID $C_8H_7NO_4$ *i.e.* $C_6H_3(NH_2)(CO_2H)_2$ [1:2:3].

Salt.—$H_2A''HSnCl_3$ 2aq: needles, got from nitro-phthalic acid by tin and HCl. The hydrochloride gives off CO_2 on evaporation, becoming *m*-amido-benzoic acid (Miller, *A.* 208, 245).

Ethyl ether Et_2A''. Oil; got by reducing ethyl *con*-nitro-phthalate.

Amido-phthalic acid $C_6H_3(NH_2)(CO_2H)_2$ [1:3:4]. Its hydrochloride splits up, like that of the preceding acid, into CO_2 and *m*-amido-benzoic acid (M.).

Ether Et_2A'' [95°] (M.). Got by reducing *u*-nitro-phthalic ether (M.; Koenigs, *B.* 10, 125). Monoclinic prisms (from alcohol). Ethereal solutions show faint blue fluorescence.

Acetyl derivative [122°]. Minute laminæ.

Amido-iso-phthalic acid $C_8H_7NO_4$ 2aq. [above 300°]. S. ·104 at 15°; ·92 at 99°.

Formed by reducing nitro-iso-phthalic acid, [249°] (Storrs a. Fittig, *A.* 158, 285; Beyer, *J. pr.* [2] 25, 491). Prisms (from alcohol) or plates (from water). Solutions give a deep reddish-brown colour with Fe_2Cl_6.

Salts: K_2A''; gives no pps. with salts of Ca or Ba, but pps. with salts of Zn, Cd, Cu, Ag, Pb, and Hg.—Na_2A''.—$MgA''4\frac{1}{2}aq$: S. 20 at 15°.—$CaA''3\frac{1}{2}aq$: S. 7·4 at 15°.—$SrA''aq$: S. 8·6 at 15°.—$BaA''1\frac{1}{2}aq$: S. 5·43 at 15°.—ZnA''.—CdA''.—$AgHA''$.—$H_2A''HCl\,aq$.—$(H_2A''HCl)_2PtCl_4 3\frac{1}{2}aq$: crystals grouped in stars.—$H_2A''HBr$.—$H_2A''HNO_3 1\frac{1}{2}aq$.

Methyl ether Me_2A'' [176°]; solidifies at 164°.

Ethyl ether Et_2A'' [118°]; solidifies at 113°. Prepared by treating a mixture of nitro-iso-phthalic ether (50 g.), alcohol (300 g.), and conc. HCl (500 g.), with zinc dust at 0°. Tufts of thin plates (from alcohol) or slender needles arranged in crosses (from water). V. sl. sol. water. Solutions fluoresce violet-red.

Amido-tere-phthalic acid $C_8H_7NO_4$ *i.e.* $C_6H_3(NH_2)(CO_2H)_2$ [2:1:4]. Obtained by reducing nitro-terephthalic acid with tin and HCl (Warren de la Rue a. Hugo Müller, *Pr.* 11, 112). Thin lemon-yellow prisms; v. sl. sol. cold water, alcohol, ether, or chloroform. Decomposed by heat without previous fusion. Its solution fluoresces blue.

Di-methyl ether Me_2A'' [126°]. Salts: $Me_2A''HCl$: white needles, saponified by water.—$(Me_2A''HCl)_2PtCl_4$ (Ahrens, *B.* 19, 1636).

Di-amido-terephthalic acid $C_8H_8N_2O_4$ *i.e.* $C_6H_2(NH_2)_2(CO_2H)_2$ [3:6:1:4].

Ether Et_2A'' [168°]. Formed by the action of bromine upon di-amido-di-hydro-terephthalic ether (di-imide of succino-succinic ether) dissolved in strong H_2SO_4. Glistening orange needles. Sparingly soluble in alcohol and ether with a yellow fluorescence. By diazotisation and treatment with Cu_2Cl_2 it is converted into di-chloro-terephthalic ether, which is reduced by sodium-amalgam to terephthalic ether. The sulphate forms very sparingly soluble colourless needles (Baeyer, *B.* 19, 430).

AMIDO-PHTHALIDE $C_8H_7NO_2$ *i.e.* $C_6H_3(NH_2)\langle{}^{CO}_{CH_2}\rangle O \left[4:{}^{1}_{2}\right]$. [178°]. Formed by reducing nitro-phthalide [141°] (Hoenig, *B.* 18, 3448). Short prisms; sol. chloroform, sl. sol. alcohol, ether, and benzene, v. sl. sol. cold water. Salts: B'HCl: needles.—$B'_2H_2PtCl_6$.

DI-AMIDO-ISO-PHTHALOPHENONE $C_{20}H_{16}N_2O_2$. Two isomeric compounds of this formula are obtained by reducing the two di-nitro-phthalophenones that are got by nitrating iso-phthalophenone $C_6H_4(CO.C_6H_5)_2$ [1:3] (Ador, *Bl.* [2] 33, 56).

AMIDO-PODOCARPIC ACID *v.* PODOCARPIC ACID.

DI-AMIDO-PROPANE *v.* TRIMETHYLENE-DIAMINE and PROPYLENE-DIAMINE.

(3:4:1)-AMIDO-PROPENYL-BENZOIC ACID $C_{10}H_{11}NO_2$ *i.e.* $C_6H_3(NH_2)(C_3H_5)CO_2H$ [3:4:1] [94°].

Formation:—1. By reduction of nitro-propenyl-benzoic acid with $FeSO_4$ and NH_3.—2. By boiling amido-oxypropyl-benzoic acid with HCl (Widman, *B.* 16, 2572). Long white needles. Easily soluble in alcohol, ether, and benzene, sparingly in water and ligroine. Tolerably marked basic properties.

Salts: A'H,HCl; long colourless easily soluble prisms.—$(A'H,HCl)_2PtCl_4$; easily soluble yellow needles.—A'H, AcOH: colourless prisms, [c. 160°].

Acetyl derivative $C_6H_3(NHAc)(C_3H_5)CO_2H$—[212°], long white needles, sl. sol. hot water. By the action of nitrous acid it is converted into methyl-cinnoline carboxylic acid $CO_2H.C_6H_3\langle{}^{CMe:CH}_{N\ :\ N}\rangle$, di-azo-propenyl-benzoic acid, $CO_2H.C_6H_3\langle{}^{CMe:CH_2}_{N:N.OH}$, probably being the intermediate product (Widman, *B.* 17, 722).

Amido-propenyl-benzoic acid $C_6H_3(NH_2)(C_3H_5)CO_2H$ [2:4:1]. [165°]. Formed by heating amido-oxypropyl-benzoic acid with dilute HCl (Widman, *B.* 19, 272). Yellow plates.

Acetyl derivative: [122°]; white prisms.

α-AMIDO-PROPIONAMIDE $C_3H_8N_2O$ *i.e.* $CH_3.CH(NH_2).CO.NH_2$. [above 250°]. Occurs in urine (Baumstark, *A.* 173, 342). Small columns, sl. sol. cold water, m. sol. hot water, insol. ether insol. alcohol (difference from urea). Converted by nitrous acid into sarco-lactic acid, and by baryta-water at 150° into CO_2, NH_3, and ethylamine.

α-AMIDO-PROPIONIC ACID *v.* ALANINE.

β-Amido-propionic acid $C_3H_7NO_2$ *i.e.* $CH_2(NH_2).CH_2.CO_2H$. [180°]. Mol. w. 89.

Formation.—1. Together with β-imido-propionic acid, by the action of NH_3 upon β-iodo-propionic acid (Heintz, *A.* 156, 36; Mulder, *B.* 9, 1903).—2. From cyano-acetic acid by reduction with Zn and H_2SO_4 (Engel, *B.* 8, 1597).

Properties.—Prisms; v. e. sol. water, sl. sol. alcohol. Sweet taste. Split up by distillation into NH_3 and acrylic acid.

Salt.—$CuA'_2 5aq$: dark-blue prisms.

(α)-AMIDO-PROPIONITRILE $C_3H_6N_2$ *i.e.* $CH_3.CH(NH_2).CN$. A mixture of aldehyde-ammonia and prussic acid (30 p.c. solution) is acidified with H_2SO_4Aq (1:3) (Erlenmeyer a. Passavant, *A.* 200, 121). Liquid; quickly changes to imido-propionitrile, giving off NH_3.—B'HCl.—$B'_2H_2PtCl_6$.

AMIDO-PROPYL-ALCOHOL *v.* OXY-PROPYL-AMINE.

AMIDO-ISOPROPYL-BENZOIC ACID AMIDO-CUMINIC ACID.

AMIDO-n-PROPYL-CINNAMIC ACID $C_{12}H_{15}NO_2$ *i.e.* $C_6H_3(C_3H_7)(NH_2).C_2H_2.CO_2H$ [4:2:1] [155°]. Formed by reduction of nitro-*n*-propyl-cinnamic acid with $FeSO_4$ and NH_3 (Widman, *B.* 19, 277). Glistening yellow needles. Easily soluble in hot alcohol. By heating with dilute HCl for a long time it is converted into *n*-propyl-carbo-styril [162°].

α-AMIDO-p-PROPYL-PHENYL-ACETIC ACID $C_{11}H_{15}NO_2$ *i.e.* $C_3H_7.C_6H_4.CH(NH_2).CO_2H$. [197°]. Prepared by saponifying the product of the action of HCN upon cumin-hydramide (Plöchl, *B.* 14, 1316). Sl. sol. cold water, insol. alcohol and ether.

AMIDO-PYRENE *v.* PYRENE.

AMIDO-PYROCATECHIN $C_6H_7NO_2$ *i.e.* $C_6H_3(NH_2)(OH)_2$. By reducing the nitro-compound by Sn and HCl.

Salt: B'HCl: dark needles. Sodic car-

bonate liberates the free base which, however, is rapidly oxidised by air forming a violet solution (Benedikt, *J. pr.* [2] 18, 457; *B.* 11, 363).

Methylene derivative $C_7H_7NO_2$ *i.e.* $H_2N.C_6H_3<{O \atop O}>CH_2$. Obtained by reducing methylene - nitro - pyrocatechin or nitro-piperonylic acid (Hesse, *A.* 199, 341). Brownish oil. Salt: B'HCl.

AMIDO-PYROGALLOL $C_6H_7NO_3$ *i.e.* $C_6H_2(NH_2)(OH)_3$. *Amido-pyrogallic acid.* From the nitro-compound. Its alkaline solution turns blue in air.

Salt.—B'HCl: needles (Barth, *M.* 1, 884).

AMIDO-PYRO-MECONIC ACID $C_5H_5NO_3$ *i.e.* $C_5H_3(NH_2)O_3$. From nitro-pyro-meconic acid, tin and HCl (Ost, *J. pr.* [2] 19, 194). Needles (from water). Fe_2Cl_6 gives a blue colour, changed to red by excess.—B'HCl aq.

Di-amido-pyro-mellitic ether $C_6(NH_2)_2(CO_2Et)_4$ [134°]. From the nitro compound (Nef, *A.* 237, 24). *Diacetyl derivative* [149°].

(a)-AMIDO-PYRRYL METHYL KETONE $C_6H_8N_2O$ *i.e.* $C_4H_3(NH_2)N.CO.CH_3$. Formed by reduction of (a)-nitro-pyrryl methyl ketone with tin and HCl (Ciamician a. Silber, *B.* 18, 1460).—$B'_2H_2PtCl_6$: long yellow needles.

(*B.* 4)-AMIDO-QUINOLINE $C_9NH_6.NH_2$. [67°].

Preparation.—1. By reducing nitro-quinoline, [89°] (Koenigs, *B.* 12, 451).—2. By heating oxy-quinoline with zinc-chloride-ammonia (Bedall a. Fischer, *B.* 14, 2573). Plates. Dissolves in acids. CrO_3 gives a blood-red colour.

(*B.* 2)-**Amido-quinoline** $C_9H_8N_2$ [114°]. Prepared by reduction of nitro-quinoline from *p*-nitraniline (La Coste, *B.* 16, 670). Colourless plates or flat needles (containing 2aq). Sublimable. V. sol. alcohol and ether, less in water and ligroïn. Salts: B''HCl: large colourless prisms.—$B''_2H_2Cl_2PtCl_4$ 2aq.: crystalline pp.

Picrate $B''(C_6H_2(NO_2)_3OH)_2$: needles.

(*B.* 3)-**Amido-quinoline**

$C_6H_3(NH_2)<{CH:CH \atop N=CH}>$. [110°]. Prepared by heating (*B.* 3)-oxy-quinoline with ammoniacal $ZnCl_2$ (Riemerschmied, *B.* 16, 725). Yellow plates. Sublimable. Sol. alcohol, ether, and hot water; sl. sol. cold water. The *picrate* forms long red needles, v. sl. sol. ether.

(*a*)-**Di-amido-quinoline** $C_9H_9N_3$ *i.e.* $C_9H_5(NH_2)_2N$. [156° uncorr.]. Formed by reduction of (*a*)-di-nitro-quinoline [183°] with $SnCl_2$ (Claus a. Kramer, *B.* 18, 1247). Thick yellowish needles.—$B''H_2Cl_2PtCl_4$: red needles.

(*β*)-**Di - amido - quinoline.** [163° uncorr.]. Formed by reduction of (*β*)-di-nitro-quinoline [184°] with $SnCl_2$ (C. a. K.). Small yellow needles or plates. Is not sublimable or volatile with steam. V. sol. water and alcohol, sl. sol. ether, benzene, and ligroïn.—$B_2H_2Cl_2PtCl_4$: yellow crystalline powder.

DI-AMIDO-QUINONE $C_6H_2(NH_2)_2O_2$ [6:2:4:1].

Diacetyl derivative $C_6H_2(NHAc)_2O_2$: [265°–270°]. Formed by oxidation of tetra-acetyl-di-amido-hydroquinone $C_6H_2(NHAc)_2(OAc)_2$ or tri-acetyl-tri-amido-phenol $C_6H_2(NHAc)_3OH$ (from picric acid). By heating with $SnCl_2$ dissolved in conc. HCl it yields di-amido-hydroquinone (Nietzki a. Preusser, *B.* 19, 2247; 20, 797).

DI-AMIDO-QUINONE-IMIDE *v.* AMIDO-DI-IMIDO-PHENOL.

(*B.* 2)-**AMIDO-QUINOXALINE** $C_8H_7N_3$ *i.e.* $C_6H_3(NH_2)<{N:CH \atop N:CH}>$ [159°]. Formed by condensation of glyoxal with (1:2:4)-tri-amido-benzene (Hinsberg, *B.* 19, 1254). Yellow needles or large crystals. Sublimable. V. sol. water, alcohol, and chloroform, m. sol. ether and benzene. The ethereal and chloroform solutions have a yellowish-green fluorescence. The aqueous solution gives yellow pps. with $AgNO_3$ and $HgCl_2$. Its solution in HCl is deep violet.

Salts.—B'HCl: brown plates with green reflection.—$B'_2H_2SO_4$.—$B'_2H_2Cl_2PtCl_4$.

AMIDO-RESORCIN $C_6H_7NO_2$ *i.e.* [1:2:4] $C_6H_3(NH_2)(OH)_2$. Formed by reducing nitro-resorcin with tin and HCl (Weselsky, *A.* 164, 6).—B'HCl 2aq: gives brown colour with Fe_2Cl_6. The free base is unstable.

Ethers: $C_6H_3(NH_2)(OEt)_2$: [32°]; (251°). From benzene-azo-di-ethyl-resorcin (Will a. Pukall, *B.* 20, 1124).—$C_6H_3(NH_2)(OH)(OEt)$. [148°].

Amido-resorcin. *Ethyl ether* $C_6H_3(NH_2)(OEt)_2$ [1:2:6]. [124°]. From benzene-*o*-azo-di-ethyl-resorcin (Pukall, *B.* 20, 1148).

Di-amido-resorcin $C_6H_8N_2O_2$ *i.e.* $C_6H_2(NH_2)_2(OH)_2$. [1:3:4:6]. The hydrochloride is obtained by reducing dinitroso-resorcin (Fitz, *B.* 8, 633) or benzene-disazo-resorcin (Liebermann a. Kostanecki, *B.* 17, 881). It gives a blue colour with Fe_2Cl_6. The free base is unstable. If the hydrochloride is suspended in chloroform, a little aqueous NaOH added, and then a large quantity of water, a beautiful blue colour is produced.—$B''H_2SO_4$ 1½aq.

Di-amido-resorcin. Formed by reduction of di-nitro-resorcin with tin and HCl (Typke, *B.* 16, 555). The hydrochloride ($B''H_2Cl_2$) forms easily soluble flat needles. Fe_2Cl_6 produces a ppn. of steel-blue prisms of di-imido-resorcin.

AMIDO-SALICYLIC *v.* OXY-AMIDO-BENZOIC.

DI - AMIDO - STILBENE *v.* DI-AMIDO-DI-PHENYL-ETHYLENE.

AMIDO-STRYCHNINE $C_{21}H_{23}N_3O_2$ *i.e.* $C_{21}H_{21}(NH_2)N_2O_2$. [275°]. (c. 280°) at 5 mm. From nitro-strychnine and $SnCl_2$ (Loebisch a. Schoop, *M.* 6, 848). Cubes (from alcohol). Insol. water, sl. sol. benzoline, m. sol. alcohol, v. e. sol. ether and chloroform. Its salts are very much more soluble than those of strychnine; they turn reddish-violet in moist air. They give the general reactions for alkaloids. Give no colour with conc. H_2SO_4 and $K_2Cr_2O_7$. A dilute acid solution is turned blue by aqueous $K_2Cr_2O_7$ or by Fe_2Cl_6. Salts.—B''2HCl: prisms.—$B''H_2PtCl_6$.

Acetyl derivative $C_{21}H_{21}(NAcH)N_2O_2$ aq [205°] (L. a. S. *M.* 7, 77).

Di - amido - strychnine $C_{21}H_{20}(NH_2)_2N_2O_2$. [263°]. From di-nitro-strychnine, tin, and HCl (Hanriot, *C. R.* 96, 586; *Bl.* [2] 41, 236). Prisms (from chloroform); v. sl. sol. water and ether, m. sol. alcohol, v. sol. chloroform. Gives no colour with conc. H_2SO_4 and $K_2Cr_2O_7$. A dilute acid solution is turned violet-blue by oxidising agents such as $K_2Cr_2O_7$Aq or NaOCl.

p-**AMIDO-STYRENE** C_8H_9N *i.e.* $C_6H_4(NH_2).CH:CH_2$. [76°–81°]. A body of this composition is formed by reducing *p*-nitro-

cinnamic acid with tin and HCl (Bender, *B.* 14, 2359), and by heating *p*-amido-cinnamic acid (Bernthsen a. Bender, *B.* 15, 1982).—$B'_2H_2PtCl_6$.

o-**AMIDO-STYRYL-ACRYLIC ACID** $C_{11}H_{11}NO_2$ *i.e.* $C_6H_4(NH_2).CH:CH.CH:CH.CO_2H$. *o-Amido-cinnamenyl-acrylic acid.* [177°]. Formed by reduction of *o*-nitro-styryl-acrylic acid with ferrous sulphate and ammonia. Yellow needles. V. sol. chloroform, ether, alcohol, and acetic acid, sl. sol. CS_2 and hot water, v. sl. sol. cold water. Its ethereal solution has a green fluorescence. It forms salts with acids and with bases. The hydrochloride is easily soluble, the sulphate sparingly soluble. The salts with bases are deep yellow.

Acetyl derivative $C_6H_4(NHAc).C_4H_4.CO_2H$: [253°]. Small white tables, sol. hot alcohol, sl. sol. cold alcohol and ether, insol. water (Diehl a. Einhorn, *B.* 18, 2332).

o-**AMIDO-STYRYL-PROPIONIC ACID** $C_6H_4(NH_2).CH:CH.CH_2.CH_2.CO_2H$. *o-Amido-cinnamyl-acetic acid.* [59° hydrated]. Crystals (+H_2O). Easily soluble in ordinary solvents. Formed by reduction of *o*-amido-styryl-acrylic acid with sodium-amalgam (Diehl a. Einhorn, *B.* 20, 378).

AMIDO-SUCCINAMIC ACID *v.* ASPARAGINE.

AMIDO-SUCCINIC ACID *v.* ASPARTIC ACID.

Di-amido-succinic acid $C_4H_8N_2O_4$ *i.e.* $CO_2H.CH(NH_2).CH(NH_2).CO_2H$. [125°].

Formation.—1. From di-bromo-succinic acid and NH_3 (Lehrfeld, *B.* 14, 1817).—2. By reducing the di-phenylhydrazide of di-oxy-tartaric acid, $CO_2H.C(N_2HPh).C(N_2HPh).CO_2H$, in alkaline solution with sodium amalgam. The yield is 35 p.c. of the theoretical (Tafel, *B.* 20, 247).

Properties.—Prisms; v. sl. sol. water, alcohol, ether, acetone, acetic acid, chloroform, aniline, phenol, and CS_2. Sol. aqueous acids and alkalis.

Di-amido-succinic acid $C_4H_8N_2O_4$. [151° uncorr.]. White needles or prisms. Sol. water, alcohol, and ether. The acid is isomeric with the preceding. The ether is formed by the action of NH_3 on di-chloro-succinic ether.

Diethyl-ether $A''Et_2$. [122° uncorr.] Colourless needles or trimetric prisms. Sol. alcohol and ether, v. sl. sol. water.

Salts.—$A''Ag_2$ and $A''Pb$: insol. pps.—$A''Cu$: green pp.

Di-amide $C_2H_6N_2(CO.NH_2)_2$. [160° uncorr.]. Long slender needles. Insol. water and ether (Claus a. Helpenstein, *B.* 14, 624; 15, 1850).

AMIDO-SUCCINURIC ACID *v.* URAMIDO-SUCCINIC ACID.

AMIDO-SULPHOBENZIDE *v.* AMIDO-DI-PHENYL SULPHONE.

AMIDO-SULPHO-BENZOIC ACID $C_7H_7NSO_5$ *i.e.* $C_6H_3(NH_2)(SO_3H)(CO_2H)$ [1:3:5]. From nitro-*m*-sulpho-benzoic acid and aqueous ammonium sulphide (Limpricht a. Uslar, *A.* 106, 29). Needles, v. sol. hot water, m. sol. alcohol, v. sl. sol. ether. Blackened by heat. Combines with bases but not with acids.

(*a*)-amido-sulpho-benzoic acid $C_7H_7NSO_5aq$ *i.e.* $C_6H_3(NH_2)(SO_3H)(CO_2H)$ [1:*x*:5]. Obtained, together with the following acid, by sulphonation of *m*-amido-benzoic acid (Griess, *J. pr.* [2] 5, 244). Four-sided laminæ, m. sol. hot water.—Salt:—$BaA''2aq$: v. sl. sol. water.

(*β*)-amido-sulpho-benzoic acid $C_7H_7NSO_5$ *i.e.* $C_6H_3(NH_2)(SO_3H)(CO_2H)$ [1:*x*:5]. Six-sided laminæ; v. sl. sol. hot water.—Salt: $BaA''3aq$: m. sol. water.

Amido-sulpho-benzoic acid $C_6H_3(NH_2)(SO_3H)(CO_2H)$ [1:3:6]. Rhombic plates, sol. hot water. Dilute solutions show blue fluorescence (Hart, *Am.* 1, 363).

Amido-sulpho-benzoic acid $C_6H_3(NH_2)(SO_3H)(CO_2H)$ [1:2:4].

Imide $C_6H_3(NH_2)<\substack{SO_2\\CO}>NH$. [285°]. From the amide of *p*-nitro-toluene sulphonic acid by oxidation and reduction (Noyes, *Am.* 8, 167). Colourless crystals, v. sl. sol. water. Its solution shows dark blue fluorescence.

AMIDO-SULPHO-BENZOLIC ACID. An old name for amido-benzene sulphonic acid *v.* AMIDO-BENZENE.

AMIDO-SULPHO-PHENOLIC ACID. An old name for amido-phenol sulphonic acid *v.* AMIDO-PHENOL.

a-**AMIDO-*p*-SULPHO-PHENYL-PROPIONIC ACID** $C_9H_{11}NSO_5$ *i.e.* $SO_3H.C_6H_4.CH_2.CH(NH_2).CO_2H$. From *a*-amido-phenyl propionic acid (20 g.), conc. H_2SO_4 (30 g.) and Nordhausen acid (25 g.) (Erlenmeyer a. Lipp, *A.* 219, 209). Groups of short prisms (from water). M. sol. water, v. sl. sol. alcohol, insol. ether. Does not combine with HCl. Fused with KOH gives *p*-oxy-benzoic acid.—Salts: $BaA'_2 4aq$: flat prisms.

AMIDO-TEREPHTHALIC ACID *v.* AMIDO-PHTHALIC ACID.

m-**AMIDO-THIO-BENZAMIDE** $C_7H_8N_2S$ *i.e.* $C_6H_4(NH_2).CS.NH_2$. Obtained by boiling *m*-nitro-benzonitrile with aqueous ammonium sulphide (Hofmann, *Pr.* 10, 598; *B.* 1, 197). Needles (from water). Weak base. Decomposed by heat into H_2S and amido-benzonitrile. Alcoholic solution of iodine converts it into $C_{14}H_{12}N_4S$, crystallising from water in slender needles [129°]. Forms a platino-chloride $C_{14}H_{12}N_4SH_2PtCl_6$ (Wanstrat, *B.* 6, 332).

p-Amido-thio-benzamide [170°]. From *p*-nitro-benzonitrile and conc. H_2SO_4 (Engler, *A.* 149, 299). Crystals; m. sol. alcohol.

AMIDO-THIO-CRESOL *v.* AMIDO-TOLYL MERCAPTAN.

AMIDO-THIOPHENE $C_4SH_3(NH_2)$. Prepared by reducing nitro-thiophene with tin and alcoholic HCl (Stadler, *B.* 18, 1490, 2316). Yellow oil. Very unstable; being changed in 12 hours into a brittle resin. The hydrochloride reacts with diazo salts forming stable azo compounds. Salts.—$B'HCl$.—$B'_2H_2SnCl_4$.

a-**AMIDO-THIENYL-ACETIC ACID** $C_6H_7SNO_2$ *i.e.* $C_4SH_3.CH(NH_2).CO_2H$. Formed by reducing the oxim of thienyl-glyoxylic acid $C_4SH_3.C(NOH).CO_2H$ with tin and HCl (Bradley, *B.* 19, 2115). Plates or grains; decomposes at 235°-240°. Salts.—The acid gives pps. with salts of Cu, Hg, Bi, and Zn, but no pps. with salts of Fe, Mg, Mn, Ur, Ni, Ba, Ca, Sn, or Pb.—CuA'_2aq.—$HA'HCl$.

AMIDO-THIOPHENOL *v.* AMIDO-PHENYL MERCAPTAN.

AMIDO-THYMOL $C_{10}H_{15}NO$ *i.e.* $C_6H_2Pr(NH_2)(CH_3)(OH)$ [1:3?:4:6]. Nitroso-thymol, prepared from sodium-thymol, KNO_2 and H_2SO_4 (Schiff, *B.* 8, 1500), is reduced by Sn and HCl to the well-crystallised tin salt of *p*-amido-thymol. This is dissolved in water and

decomposed by H_2S (Andresen, *J. pr.* 131, 169).—**Salt**: B'HCl: decomposes at 210°–215°.

Reactions.—1. *Bleaching powder* solution converts it into thymo-quinone-chloro-imide (*q. v.*).—2. A solution of *bromine* in NaOH oxidises it to thymo-quinone.—3. *Bromine water* has the same effect.

Amido-thymol sulphonic acid $C_{10}H_{14}(SO_3H)NO$ is among the products of the action of conc. $NaHSO_3Aq$ upon thymoquinone-chloro-imide (A.). Needles or prisms.

Di-amido-thymoquinone $C_{10}H_{14}N_2O_2$ *i.e.* $C_6PrMe(NH_2)_2O_2$ or *Oxy-amido-thymo-quinon-imide* $C_6PrMe(NH_2)(OH){<}\begin{matrix}O\\ |\\ NH\end{matrix}$. Formed by heating phenylamido-oxy-thymoquinone with alcoholic NH_3 at 100° (Anschütz a. Leather, *C. J.* 49, 725). Dark blue crystals, insol. water, ether, benzene, chloroform, and CS_2; v. sl. sol. alcohol; sol. glacial HOAc (crystallising with $\frac{1}{2}$HOAc); v. sol. HClAq, forming a red solution.

AMIDO-TOLUENE *v.* TOLUIDINE and BENZYL-AMINE.

Di-amido-toluene *v.* TOLYLENE-DIAMINE and AMIDO-BENZYLAMINE.

TRI-AMIDO-TOLUENE $C_7H_{11}N_3$ *i.e.* $C_6H_2Me(NH_2)_3$ [1:3:4:5].

p-Acetyl derivative $C_6H_2Me(NHAc)(NH_2)_2$ [1:4:3:5] [c. 264°]; pearly rods (containing aq); sol. acetic acid and hot alcohol, insol. water, ether, and benzene. Formed by reduction of acetyl-di-nitro-*p*-toluidine (1 pt.) with tin (3 pts.) and conc. HCl (8 pts.). The hydrochloride (B'HCl $\frac{1}{2}$aq) forms white concentric easily soluble needles (Niementowski, *B.* 19, 716).

Benzoyl derivative $C_6H_2Me(NHBz)(NH_2)_2$ [1:4:3:5] [c. 185°]. Formed by reducing benzoyl-di-nitro-*p*-toluidine (Hübner, *A.* 208, 318). Insol. water, sol. alcohol and ether. Salts.—B''2HCl.—$B''H_2SO_4$.

Tri-amido-toluene $C_6H_2(CH_3)(NH_2)_3$ [1:2:4:?]. Very oxidisable crystalline solid. Tri-acid base. Prepared by reduction of nitro-tolylene-*m*-diamine. $B'''(HCl)_3$ and $B'''_2(H_2SO_4)_3$ are white crystalline solids (Ruhemann, *B.* 14, 2657).

AMIDO-TOLUENE SULPHINIC ACIDS $C_7H_9NSO_2$.

***o*-Amido-toluene sulphinic acid** $C_6H_3Me(NH_2)SO_2H$ [1:2:4]. *o-Toluidine sulphinic acid.* S. ·148. From *o*-amido-toluene thio-sulphonic acid and sodium amalgam (Paysan, *A.* 221, 361). Rectangular tables, sl. sol. water or alcohol, insol. ether or benzene. At 160° it decomposes without melting.

Reactions.—1. With yellow *ammonic sulphide* forms amido-toluene thiosulphonic acid.—2. $KMnO_4$ forms amido-toluene sulphonic acid.—3. Boiling HCl forms the isomeric toluene sulphamine.—4. *Nitrous acid* forms a diazo compound which when warmed with alcohol forms the ethyl derivative of cresol sulphonic acid.

Salts.—KA'.—$BaA'_2$2aq.—AgA'.

Toluene sulphamine $C_7H_9NSO_2$. [175°]. Got by heating *o*-amido-toluene sulphinic acid with HCl and ppn. by NH_3. Needles in stars (from alcohol).—B'HCl: groups of slender needles.

***p*-Amido-toluene sulphinic acid** $C_7H_9NSO_2$ *i.e.* $C_6H_3(NH_2)Me.SO_2H$ [1:4:5]. From $C_6H_3(NH_2)Me(SO_2SH)$ by boiling with HCl but since much then changes to toluene sulphamine it is better to reduce it with sodium amalgam (Heffter, *A.* 221, 347). Hard prisms. Does not melt below 240°. Insol. alcohol, sl. sol. cold water, v. sol. hot water.

Reactions.—1. Warmed with a solution of *sulphur in ammonic sulphide* it changes to the thiosulphonic acid, $C_6H_3(NH_2)Me.(SO_2SH)$.—2. *Bromine* converts it into amido-toluene sulphonic acid.—3. Not reduced by Sn and HCl.

Salts.—KA'.—BaA'_2xaq.

Toluene sulphamine (isomeric with the above). [132°]. Got by heating *p*-amido-toluene sulphinic acid with conc. HCl. It is a base. Microscopic prisms (got by adding NH_3 to its solution in HCl). V. sol. alcohol and ether, but separates from them in a resinous form; sl. sol. water. Dissolved by treatment with water and sodium amalgam (not NaOH alone) forming sodic amido-toluene sulphinate.

Salts.—B'HCl: sl. sol. HCl, v. sol. water or alcohol.—$B'_2H_2SO_4$.—B'HBr: changes readily into amido-toluene sulphonic acid.—$B'HNO_3$: warmed with HNO_3 forms amido-toluene sulphonic acid.

Di-amido-toluene sulphinic acid $C_7H_{10}N_2SO_2$ *i.e.* $C_6H_2Me(NH_2)_2SO_2H$. *Tolylene-di-amine sulphinic acid.* S. ·047 at 20°. From $C_6H_2Me(NH_2)_2SO_2SH$ by boiling with HCl (Perl, *B.* 18, 70). Silky needles (containing aq). V. sl. sol. water, insol. alcohol, ether, and glacial HOAc.—PbA'_2 2aq: minute needles.

AMIDO-TOLUENE SULPHONIC ACIDS $C_7H_9NSO_3$ (Limpricht, *B.* 18, 2172).

***o*-Amido-toluene sulphonic acid** $C_6H_3Me(NH_2)SO_3H$aq [1:2:5]. *o-Toluidine sulphonic acid.* S. 2·76 at 12° (H. Hasse).

Preparation.—1. By heating the acid sulphate of *o*-toluidine at 220°–230°, or in a metal dish till solid (Nevile a. Winther, *C. J.* 37, 626; *B.* 13, 1941; Gerver, *A.* 169, 374; Pagel, *A.* 176, 292).—2. By reducing the corresponding nitro acid (Foth, *A.* 230, 306).

Salts.—KA'aq: tables and prisms.—NaA'4aq: tables.—$BaA'_2$7aq: tables and prisms.—AgA': prisms.

Reactions.—1. *Bromine water* forms first $CH_3.C_6H_2Br(NH_2)SO_3H$ [1:3:2:5] then di-bromo-toluidine $C_6H_2(CH_3)(NH_2)Br_2$[1:2:3:5][46°] is ppd. 2. Fused with *alkalis* or heated with water or aqueous HCl to 190° it forms *o*-toluidine.—3. *Nitrous acid* and alcohol give *m*-toluene sulphonic acid.—4. With *o-toluidine* at 235° it forms a red dye.

***o*-Amido-toluene sulphonic acid** $C_6H_3Me(NH_2)(SO_3H)$ [1:2:3]. Obtained by reducing the corresponding nitro acid (Pechmann, *A.* 173, 215). Minute needles; sl. sol. cold water. Gives *o*-toluidine when fused with KOH.

***o*-Amido-toluene sulphonic acid** $C_6H_3Me(NH_2)(SO_3H)$aq [1:2:4]. From the nitro acid (Bek, *Z.* 1869, 211; Beilstein a. Kuhlberg, *A.* 155, 21; Weckwarth, *A.* 172, 193; Hayduck, *A.* 172, 204; 174, 343; Herzfield, *B.* 17, 904). Long needles or four-sided prisms. S. ·974 at 11°; insol. alcohol. The aqueous solution is turned violet by Fe_2Cl_6. Potash-fusion gives *o*-amido-benzoic acid. Bromine gives di-bromo-toluidine sulphonic acid. **Salts.**—NaA'4aq.—KA'aq.—$BaA'_2$2$\frac{1}{2}$aq.—PbA'_2.

Amide. — $C_6H_3Me(NH_2)SO_2NH_2$. [175°]. S. ·22 at 23°. From $C_6H_3Me(NO_2)SO_2NH_2$

[128°], NH_3, and H_2S (Paysan, *A.* 221, 210). Four-sided columns.

Salt.—$C_6H_3Me(NH_3Cl).SO_2NH_2$. [240°].

***m*-Amido-toluene sulphonic acid**

$C_6H_3Me(NH_2)SO_3H$ [1:3:2]. *m-Toluidine sulphonic acid* [275°]. By sulphonation of *m*-toluidine (Lorenz, *A.* 172, 185). Tables or plates; sl. sol. water. Bromine-water produces tri-bromo-toluidine.

Salts.—$BaA'_2$9aq.—$PbA'_2$3½aq.

***m*-Amido-toluene sulphonic acid**

$C_6H_3Me(NH_2)SO_3H$aq. S. (dry) ·14 at 19°. From bromo-toluene sulphonic acid $C_6H_3MeBrSO_3H$ [1:2:4] by nitration and reduction (Hayduck, *A.* 174, 350). Minute needles.

***p*-Amido-toluene *exo*-sulphonic acid**

$C_6H_4(NH_2).CH_2.SO_3H$ [1:4]. *p-Amido-benzyl-sulphonic acid.* S. ·097 at 10°. Formed by reducing the nitro acid by NH_3 and H_2S (Mohr, *A.* 221, 219). Prisms, insol. alcohol, sl. sol. cold water.

Salts.—KA′2½aq. - $BaA'_2$8aq.

The **diazo derivative**, $C_6H_4 < \genfrac{}{}{0pt}{}{N_2}{CH_2.SO_3} >$ is converted into $C_6H_4(OEt).CH_2.SO_3H$ by heating with alcohol under 1100 mm. pressure.

***p*-Amido-toluene sulphonic acid**

$C_6H_3Me(NH_2)SO_3H$aq [1:4:2]. *p-Toluidine sulphonic acid.* S. ·45 at 20°. A product of sulphonation of *p*-toluidine (Sell, *A.* 126, 155; Malycheff, *Z.* 1869, 212); formed also by reducing *p*-nitro-toluene sulphonic acid (Beilstein a. Kuhlberg, *A.* 172, 230). Rhombohedra (containing aq). Reduces warm ammoniacal $AgNO_3$. Its aqueous solution is turned red by Fe_2Cl_6 (Herzfeld, *B.* 17, 904).

Salts.—KA′.—BaA'_2aq.—PbA'_2.

Amide. — $C_6H_3Me(NH_2)SO_2NH_2$. [164°]. From $C_6H_3Me(NO_2).SO_2NH_2$ [186°] by reducing with NH_3, and H_2S (Heffter, *A.* 221, 209). **Salt:** $C_6H_3Me(NH_3Cl)SO_2NH_2$; converted by conc. HCl and nitrous acid into $C_6H_3MeCl.SO_2NH_2$ [138°].

***p*-Amido-toluene sulphonic acid**

$C_6H_3Me(NH_2)SO_3H$ [1:4:3]. S. 10.

Preparation.—1. By sulphonating *p*-toluidine at 180°; the preceding acid is also formed, especially if the operation is protracted (Pechmann, *A.* 173, 195). - 2. By heating *p*-toluidine acid sulphate at 220°-240° (Nevile a. Winther, *C. J.* 37, 632).

Properties.—Yellowish crystals. Less soluble in cold water than the *o*-compound.

Reactions.—1. *Bromine* forms much di-bromo-toluidine, $C_6H_2(CH_3)(NH_2)BrBr$ [1:4:3:5], [73°] and also a bromo-toluidine sulphonic acid. 2. *Water* at 180° forms *p*-toluidine and H_2SO_4.—3. *Potash-fusion* gives *p*-oxy-benzoic acid.—4. *Nitrous ether* gives *m*-toluene sulphonic acid.

Salts.—$BaA'_2$3aq.—$PbA'_2$2aq. —AgA′.—The K salt is insol. in cold KOHAq (difference from preceding acid; Schneider, *Am.* 8, 274).

Amido-toluene-*o*-sulphonic acid

$C_6H_3Me(NH_2)(SO_3H)$ [1:x:2]. S. ·34 at 22°. From the (1, 4, 2) acid by nitration, removal of NH_2, and reduction (Pagel, *A.* 176, 305).—$BaA'_2$2½aq.—PbA'_2aq.

Amido-toluene sulphonic acid. Obtained by reducing the product of successive sulphonation and nitration of toluene (Hayduck, *A.* 177, 57).—Minute crystals (containing aq).—BaA'_2.

***o*-Amido-toluene di-sulphonic acid**

$C_7H_9NS_2O_6$ *i.e.* $C_6H_2Me(NH_2)(SO_3H)_2$ [1:2:3:5]. *o-Toluidine di-sulphonic acid.* Formed from $C_6H_3Me(NH_2)SO_3H$ [1:2:5] and fuming H_2SO_4 by heating an hour at 160° (Nevile a. Winther, *C. J.* 41, 421). Needles, grouped in stars; sol. water and alcohol.

Salts (H. Hasse, *A.* 230, 287).—BaA″3aq.—$BaH_2A''_2$3½aq. — K_2A''2aq. — Na_2A''6aq. — CaA″5aq.—PbA″2aq.—$PbH_2A''_2$6½aq.

Reactions.—1. By conversion into the *diazo compound* and subsequently boiling with HNO_3 it is converted into di-nitro-*o*-cresol $C_6H_2Me(OH)(NO_2)_2$ [1:2:3:5].—2. At about 240° it splits up into SO_3 and $C_6H_3Me(NH_2)(SO_3H)$ [1:2:5].—3. By $Cl.SO_3H$ at 230° it is changed into an isomeric acid with a salt K_2A''6aq.

***o*-Amido-toluene disulphonic acid**

$C_6H_2Me(NH_2)(SO_3H)_2$2aq [1:2:4:x]. From $C_6H_3Me(NH_2)(SO_3H)$ [1:2:4] and $ClSO_3H$ at 170° (Saworowicz, *B.* 18, 2181). Minute prisms. At 300° it decomposes into SO_3 and $C_6H_3Me(NH_2)SO_3H$[1:2:4]. **Salts.**—BaA″2aq.—CaA″2aq.

***m*-Amido-toluene disulphonic acid**

$C_6H_2Me(NH_2)(SO_3H)_2$ [1:3:2:x]. By sulphonation of *m*-toluidine (Lorenz, *A.* 172, 188). Easily splits up into SO_3 and the mono-sulphonic acid.

Salts.—$BaH_2A''_2$(?12½)aq.—PbA″2aq.

***p*-Amido-toluene-disulphonic acid**

$C_6H_2Me(NH_2)(SO_3H)_2$ [1:4:2:3]. From *p*-toluidine and fuming H_2SO_4 at 200° (Pechmann, *A.* 173, 217). Nodules; v. e. sol. water and alcohol.

Salt.- BaA″3aq: laminæ.

***p*-Amido-toluene-disulphonic acid**

$C_6H_2Me(NH_2)(SO_3H)_2$2½aq [1:4:2:x]. Formed from $C_6H_3Me(NH_2)(SO_3H)$ [1:4:2] by $ClSO_3H$ at 150° or fuming H_2SO_4 at 180° (L. Richter, *A.* 230, 331). Long silky needles, v. sol. water, sol. alcohol. At 290° it splits up into SO_3 and $C_6H_3Me(NH_2)(SO_3H)$ [1:4:2].

Salts. — BaA″aq. — $BaH_2A''_2$1½aq. — $BaH_2A''_2$½aq.—K_2A''2aq.—PbA″1½aq.

***p*-Amido-toluene-disulphonic acid**

$C_6H_2Me(NH_2)(SO_3H)_2$2aq [1:4:3:x]. Formed from $C_6H_3Me(NH_2)(SO_3H)$ [1:4:3] and H_2SO_4 or $ClSO_3H$ (L. Richter, *A.* 230, 314). Mass of minute needles (from water). With water at 140° (or dry at 200°) it splits up into SO_3 and $C_6H_3Me(NH_2)(SO_3H)$[1:4:3]. This acid is perhaps identical with that of Pechmann.

Salts.—BaA″3aq.—$BaH_2A''_2$3aq.—K_2A''2aq.—PbA″.—PbA″2aq.

Diazo derivative $C_6H_2Me(N_2SO_3)''SO_3H$. V. sol. water, insol. alcohol. KA′.—BaA'_2.—PbA'_2.

Hydrazine derivative.—From the diazo acid by $SnCl_2$.

$(C_6H_2Me(N_2H_3)(SO_3H)SO_3)_2Ba$ 2½aq. Reduces HgO, ammoniacal $AgNO_3$, Fe_2Cl_6 and Fehling solution.

Amido-toluene di-sulphonic acid

$C_6H_2(NH_2)Me(SO_3H)_2$(?2)aq. From *p*-bromo-toluene disulphonic acid by nitration, and reduction of the resulting nitro-toluene disulphonic acid (Kornatzki, *A.* 221, 198).

Di-amido-toluene *exo*-sulphonic acid

$C_7H_{10}N_2SO_3$ *i.e.* $C_6H_3(NH_2)_2CH_2SO_3H$. *Di-amido-benzyl-sulphonic-acid.* Formed by reducing $C_6H_3(NO_2)_2CH_2SO_3H$ with NH_3 and H_2S (Mohr, *A.* 221, 228). Silky needles.

Di-amido-toluene sulphonic acid

$C_6H_2Me(NH_2)_2SO_3H$ [1:2:4:5]. Formed from $C_6H_2Me(NO_2)(NH_2)SO_3H$ and $SnCl_2$ (Foth, *A.*

230, 309). Small brownish prisms, rhombohedra (from water). Salts.—HA'HCl aq: prisms, decomposed by boiling water. — HA'HBr aq.— BaA'_2 $5\frac{1}{2}$aq.—KA' aq.

o-AMIDO - TOLUENE - THIO - SULPHONIC ACID $C_7H_9NS_2O_2$ *i.e.* $C_6H_3Me(NH_2)SO_2SH$ [1:2:4]. From $C_6H_3(NO_2)MeSO_2Cl$ and ammonic sulphide (Limpricht a. Paysan, *A.* 221, 360). Four-sided prisms. Decomposes without melting at 115°. Sl. sol. cold water, insol. alcohol. Warmed with HCl forms S and toluene sulphamine. Salt.— AgA'.

p-Amido-toluene thio-sulphonic acid $C_6H_3(NH_2)Me.SO_2SH$ [1:4:5]. Formed from $C_6H_3(NO_2)MeSO_2Cl$ [44°] and ammonic sulphide (Limpricht a. Heffter, *A.* 221, 345). Hard yellowish prisms (from water). Decomposed at 120° without melting. Insol. alcohol or ether, sl. sol. water. Decomposed by HCl with deposition of S and formation of $C_6H_3(NH_2)MeSO_2H$.

Salts: $BaA'_2$2aq.—AgA'.

Di-amido-toluene thiosulphonic acid $C_7H_{10}N_2S_2O_2$ *i.e.* $C_6H_2(CH_3)(NH_2)_2.SO_2SH$. [152°].

Formation.—1. By reduction of di-nitro-toluene-sulphonic chloride with NH_4HS.—2. By reduction of di-nitro-toluene sulphinic acid with NH_4HS. Small silky prisms. V. sl. sol. water, insol. alcohol and ether.

Salts.—A'Ag: white insol. pp.—A'Na: large tables—A'_2Pb: easily soluble (Perl, *B.* 18, 67).

AMIDO-TOLUIC ACIDS $C_8H_9NO_2$. *Amido-toluylic acids.*

(*a*)-amido-*o*-toluic acid $C_6H_3Me(NH_2)CO_2H$ [1:4:2]. [196°]. Formed by reducing (*a*)-nitro-*o*-toluic acid (Jacobsen, *B.* 17, 164). Small prisms, v. sol. hot alcohol, and hot water, sl. sol. cold water. Converted by nitrous acid into oxy-toluic acid [172°].

(*β*)-amido-*o*-toluic acid $C_6H_3Me(NH_2)CO_2H$ [1:6:2] [191°]. Formed by reducing (*β*)-nitro-*o*-toluic-acid (Jacobsen, *B.* 16, 1959; 17, 164). Small needles, v. sol. cold water. Converted by nitrous acid into oxy-toluic acid [183°].

(*γ*)-amido-*o*-toluic acid $C_6H_3Me(NH_2)CO_2H$ [1:5:2]. [153°] (Hoenig, *B.* 18, 3449); [c. 165°] (J.).

Formation.—1. By reducing (*γ*)-nitro-*o*-toluic acid.—2. By heating nitro-phthalide [141°] with HI and P at 205°. Colourless needles; may be sublimed, but at 200° it splits off CO_2 forming *m*-toluidine. V. sol. hot alcohol, m. sol. hot water and ether, sl. sol. chloroform, benzene, and cold water. Nitrous acid produces oxy-toluic acid [179°].

Salts: HA'HCl: slender needles.—*CuA'_2. —$HA'H_3PO_4$: plates.

Amido-*m*-toluic acid $C_6H_3Me(NH_2)CO_2H$ [1:4:3] or [1:4:5].

Formation.—1. The hydrochloride is obtained by warming methyl-isatoic acid with HClAq (Panaotović, *J. pr.* [2] 33, 61).—2. The same acid is got from *m*-toluic acid by nitration and reduction (Jacobsen, *B.* 14, 2354; compare Panaotović, *loc. cit.*).

Properties.—Trimetric, thread-like rods (from water). Sl. sol. water, v. sol. alcohol and ether. Salt: HA'HCl. [207°]. Colourless trimetric prisms; m. sol. water and alcohol, sl. sol. ether.

Methyl ether $C_6H_3Me(NH_2)CO_2Me$. [62°]. From methyl-isatoic acid and MeOH at 180°. Slender columns; sl. sol. water.

Amide $C_6H_3Me(NH_2)CO.NH_2$. [178°]. From methyl-isatoic acid and NH_3Aq. Small columns (from water); v. sol. alcohol.

Anilide $C_6H_3Me(NH_2)CONPhH$. [240°]. Pearly tablets (from alcohol); v. sl. sol water.

Phenyl-hydrazide $C_6H_3Me(NH_2).CO.N_2H_2Ph$. [198°]. From methyl-isatoic acid and phenyl-hydrazine. Pearly crystals (from alcohol); v. sl. sol. water. Forms a violet solution with conc. H_2SO_4.

(*β*)-Amido-toluic acid $C_6H_3(CH_3)(NH_2)(CO_2H)$ [1:2:3]. [132°]. Obtained by nitration and reduction of *m*-toluic acid (Jacobsen, *B.* 14, 2354; compare Panaotović, *J. pr.* [2] 33, 61). Small flat prisms; m. sol. water.

Amido-*m*-toluic acid. *Benzoyl derivative* $C_6H_3(NHBz)MeCO_2H$ [5 or 6:1:3]. Formed by oxidation of benzoyl iso-cymidine (Kelbe a. Warth, *A.* 221, 168). Small yellowish needles (from alcohol).

DI-AMIDO-DITOLYL $C_{14}H_{16}N_2$.

Di-amido-ditolyl [4:3:1] $(NH_2)MeC_6H_3.C_6H_3Me(NH_2)$ [1:3:4]. *o-Tolidine.* [112°].

Formation.—1. By passing Cl_2O into an ethereal solution of *o*-hydrazotoluene (Petrieff, *B.* 6, 557).—2. By heating *o*-hydrazo-toluene (Petrieff, *B.* 6, 557).—3. By heating *o*-hydrazo-toluene with HCl (Schultz, *B.* 17, 467).—4. By warming an alcoholic solution of *o*-azo-toluene with $SnCl_2$ and HCl (S.).

Pearly plates; v. sol. alcohol and ether, sl. sol. water. Converted by diazo reaction into *m*-ditolyl. Converted by boiling its diazo-perbromide with alcohol, into a di-bromo-ditolyl, which oxidises to bromo-*m*-toluic acid [1:2:4], [205°]. Salts.—The sulphate and hydrochloride are sparingly soluble in water.

Acetyl derivative $C_{12}H_6Me_2(NAcH)_2$. [315° cor.]

Di-amido-ditolyl. *m-Tolidine.*

The sulphate, $B''H_2SO_4$, separates slowly when a few drops of H_2SO_4 are added to an alcoholic solution of *m*-hydrazotoluene (Goldschmidt, *B.* 11, 1626). The free base has a low melting-point. Gives a blue colour with Fe_2Cl_6.

'Di-amido-ditolyl.' [107°]. Formed by the action of SO_2 or of $SnCl_2$ and HCl upon an alcoholic solution of *p*-azo-toluene (Melms, *B.* 3, 554; Schultz, *B.* 17, 472). Silvery plates. Gives a blue colour with Fe_2Cl_6. Fischer (*B.* 25, 1019) has shown this body to be tolylene-tolyl-diamine.

Di-amido-*u*-ditolyl [4:3:1]. $(NH_2)MeC_6H_3.C_6H_3Me(NH_2)$ [1:2:4]? *o-m-Tolidine.* Formed by the action of $SnCl_2$ and HCl on an alcoholic solution of *o-m*-azo-toluene. By diazotisation in alcoholic solution it is converted into a ditolyl of boiling point 270° which on oxidation gives isophthalic acid.

Salts.—$B''H_2Cl_2$: easily soluble silky needles. —$B''H_2SO_4$*: very sparingly soluble plates (Schultz, *B.* 17, 471).

AMIDO-TOLYL-BENZAMIDINE $C_{14}H_{15}N_3$ *i.e.* $NH_2.C_6H_3Me.NH.C(NH).C_6H_5$ [212°]. From benzonitrile and (1:2,4)-tolylene-diamine hydrochloride (Bernthsen a Trompetter, *B.* 11, 1758). White needles.—B'HCl: prismatic tables.

AMIDO-TOLYL-ISO-BUTANE $C_{11}H_{17}N$ *i.e.* $C_6H_3Me(C_4H_9)NH_2$ [1:5:2]. (243°). From *o*-

toluidine and isobutyl alcohol (Effront, *B.* 17, 2320). Salts.—B'HCl.—B'HBr.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Acetyl derivative [162°]. Plates.

Benzoyl derivative [168°]. Needles.

Amido-tolyl-isobutane $C_6H_3Me(C_4H_9)NH_2$ [1:3:2]. (244°). From *o*-toluidine, isobutyl alcohol, and $ZnCl_2$ (Erhardt, *B.* 17, 419; Effront, *B.* 17, 2340). *Formyl derivative* [105°].

Acetyl derivative [142°].

***o*-AMIDO-TOLYL-ETHANE** $C_9H_{13}N$ *i.e.* $C_6H_3Me(NH_2)Et$ (230°). *Methyl-ethyl-phenyl-amine. Amido-ethyl-toluene.* From *o*-toluidine, alcohol, and $ZnCl_2$ at 270° (Benz, *B.* 15, 1650). Salts.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Acetyl derivative [106°]. (314°).

DI-AMIDO-DI-TOLYL-ETHYLENE DIAMINE *v.* DI-TOLYLENE-ETHYLENE-TETRA-AMINE.

AMIDO-TOLYL MERCAPTANS C_7H_9NS. *Amido-thio-cresols. Amido-tolyl sulphydrate.* Prepared by reducing the chlorides of the corresponding nitro-toluene sulphonic acids (Hess, *B.* 14, 488).

Amido-*o*-tolyl mercaptan $C_6H_3Me(NH_2).SH$ [1:4:2]. [42°]. Sol. alcohol, ether, alkalis, and acids; oxidised by air.

Salt.—B'HCl: prisms or tables.

Acetyl derivative [195°]: slender needles; insol. HCl.

Amido-*m*-tolyl mercaptan $C_6H_3Me(NH_2)SH$ [1:4:3]. Oil; oxidised in air gives with $HgCl_2$ a white crystalline pp.; with $Pb(OAc)_2$ a yellow amorphous pp. Gives anhydro compounds with formic acid, acetic anhydride, and benzoyl chloride.

Amido-*p*-tolyl mercaptan $C_6H_3Me(NH_2)SH$ [1:2:4]. Oil. Oxidised by air to the disulphide.

Salt.—B'HCl: short needles.

Acetyl derivative [240°].

Amido-tolyl mercaptan $C_6H_3Me(NH_2)SH$ [1:2:?] From *o*-nitro-toluene sulphochloride [36°]. Oil.

Salt.—B'HClaq: six-sided tables. Gives with Fe_2Cl_6 a pp. of the disulphide. $HgCl_2$ gives glistening plates, and alkaline lead acetate gives a yellow pp.

AMIDO-TOLYL METHYL KETONE $C_9H_{11}NO$ *i.e.* [1:2:5] $C_6H_3(CH_3)(NH_2).CO.CH_3$ [102°]. (280°-284°). Prepared by heating a mixture of *o*-toluidine (1 pt.), $ZnCl_2$ (2 pts.), and acetic anhydride (3 or 4 pts.), for 8 or 9 hours (Klingel, *B.* 18, 2696). Flat white needles. V. sol. alcohol, ether, and hot water, v. sl. sol. benzene and petroleum-ether. Salts.—B'HCl: flat white soluble prisms.—$B'_2H_2Cl_2PtCl_4$: yellow needles, v. sol. alcohol, sl. sol. hot water, insoluble ether.—$B'_2H_2SO_4$: white needles.

Acetyl derivative $C_6H_3Me(CO.Me)(NHAc)$, [144°]; white crystals; v. sol. alcohol and warm water.

AMIDO-TOLYL-(αα)-DIMETHYL-PYRROL $C_4NH_2Me_2C_6H_4NH_2$. [73°]. (322°). Obtained by heating its dicarboxylic acid (*v. infra*).

***m*-AMIDO-TOLYL-(αα)-DI-METHYL-PYRROL (ββ)-DICARBOXYLIC ACID** $C_{15}H_{16}N_2O_4$ *i.e.* $C_4NMe_2(C_7H_6NH_2)(CO_2H)_2$. From *m*-tolylene diamine, and diacetyl-succinic ether (Knorr, *A.* 236, 313). Yellow plates (containing 2aq). At 203° it gives CO_2 and *m*-amido-tolyl-(αα)-di-methyl-pyrrol. Ether Et_2A'' [134°].

AMIDO-TOLYL-OCTANE $C_{15}H_{25}N$ *i.e.* $C_6H_3Me(NH_2)C_8H_{17}$. [325°]. From *n*-octyl alcohol, *o*-toluidine, and $ZnCl_2$ at 280° (Beran, *B.* 18, 145). Salts.—B'HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Acetyl derivative [81°].

DI-AMIDO-DI-TOLYL-OXAMIDE *v.* *Oxalyl-*DI-TOLYLENE-TETRA-AMINE.

AMIDO-TOLYL SULPHYDRATE *v.* AMIDO-TOLYL MERCAPTAN.

DI-AMIDO-DI-TOLYL SULPHIDE $C_{14}H_{16}N_2S$ *i.e.* $(C_6H_3MeNH_2)_2S$ [1:4:2]. *Thio-toluidine.* [103°]. Prepared by heating *p*-toluidine, sulphur, and litharge together at 150° (Merz a. Weith, *B.* 4, 393). Laminæ (from alcohol); sl. sol. water.

Salts.—Decomposed by water.—B''2HCl sl. sol. conc. HClAq.—$B''H_2PtCl_6$.—$B''H_2SO_4$.—$B''H_2SO_4$ 2aq. — $B''H_2Br_2$. — $B''H_2I_2$. — $B''(C_6H_2(NO_2)_3OH)_2$ [179°]: silky yellow needles (from benzene); v. sl. sol. ether and cold water.

Diacetyl derivative [211°].

Dibenzoyl derivative [186°] (Truhlar, *B.* 20, 664).

Di-amido-di-*p*-tolyl sulphide ν-carboxylic ether $S(C_6H_3Me.NH.CO_2Et)_2$. *Thio-p-tolyl urethane* [113°]. From the preceding and $ClCO_2Et$. Crystals; v. sol. alcohol, ether, and benzene (T.).

AMIDO-TOLYL-UREA $C_8H_{11}N_3O$ *i.e.* $NH_2.CO.NH.C_6H_3Me.NH_2$. Formed, in small quantity, by the action of tolylene diamine sulphate on potassium cyanate (Strauss, *A.* 148, 159). V. sol. alcohol.

Di-amido-di-*p*-tolyl-urea $CO(NH.C_7H_6.NH_2)_2$. Formed by reducing the corresponding nitro-compound (A. G. Perkin, *C. J.* 37, 700). Minute satiny needles; sl. sol. alcohol.—B'' 2HCl.

AMIDO-TYROSINE $C_9H_{12}N_2O_3$ *i.e.* $C_6H_3(OH)(NH_2).C_2H_3(NH_2).CO_2H$. From nitro-tyrosine (Beyer, *Bl.* 1867, ii. 369). Crystalline powder; v. sol. water, sl. sol. alcohol.

Salts.—$B''H_2Cl_2$aq.—$B''H_2SO_4$.—$B''2H_2SO_4$.—$(B''H_2SO_4)_2ZnSO_4$.

AMIDO-URAMIDO-BENZOIC ACIDS $C_8H_9N_3O_3$ *i.e.* $NH_2.CO.NH.C_6H_3(NH_2).CO_2H$. Prepared by reducing the two nitro-uramido-benzoic acids (Griess, *B.* 5, 195).

(α)-Acid. Plates; sl. sol. water, v. sl. sol. alcohol. Salts.—HA'HCl.—AgA'.

(β)-Acid. Plates; m. sol. hot water. Forms no hydrochloride. Boiling aqueous baryta or HCl forms NH_3 and amido-carboxamido-benzoic acid, of which the barium salt, $Ba(C_8H_7N_2O_3)_2$ 4aq crystallises in needles.

(α)-AMIDO-UVITIC ACID $C_9H_9NO_4$ *i.e.* $C_6H_2(NH_2)(CH_3)(CO_2H)_2$ [2:1:3:5] (?). Colourless solid. Sl. sol. water. Prepared by reduction of (α)-nitro-uvitic acid (Böttinger, *B.* 13, 1933).

(β)-Amido-uvitic acid [c. 255°] (Böttinger, *B.* 9, 807).

AMIDO-VALERIC ACIDS $C_5H_{11}NO_2$.

α-Amido-*n*-valeric acid $CH_3.CH_2.CH_2.CH(NH_2).CO_2H$.

Formation.—1. From *n*-butyric aldehyde-ammonia and aqueous HCN (Lipp, *A.* 211, 359). 2. From its benzoyl derivative which occurs among the products of oxidation of benzoyl-coniine (Baum, *B.* 19, 506).—3. From bromo-valeric acid and NH_3Aq at 130° (Juslin, *Bl.* [2] 37, 3).

Properties.—White glistening plates; v. sol. water, sl. sol. alcohol, insol. ether; may be sublimed. Has a sweet taste. Is optically inactive. Neutral to litmus.

Salts. — HA'HCl: needles or groups of prisms; only deliquescent in very moist air. —$HA'HNO_3$. — $(HA'HCl)_2PtCl_4$. — CuA'_2: small blue plates, sl. sol. water, insol. alcohol.—AgA': crystalline pp., sl. sol. water.

γ-Amido-valeric acid
$CH_3.CH(NH_2).CH_2.CH_2.CO_2H$. [193° uncorr.]. Obtained by reduction of the phenyl-hydrazide of β-aceto-propionic acid—
$CH_3.C(N_2HPh).CH_2.CH_2.CO_2H$ in alcoholic solution with sodium amalgam and acetic acid (Tafel, *B.* 19, 2415; 20, 249). White plates. V. sol. water, nearly insol. alcohol, insol. benzene and ether. On heating it splits off H_2O and the anhydride distils. The hydrochloride forms glistenin plates, easily soluble in alcohol.

Anhydride $\overbrace{NH \text{——————}}$ $CH_3.CH.CH_2.CH_2.CO$. *Oxy-methyl-pyrrol di-hydride.* (248° i.V.) at 743 mm. colourless liquid which solidifies in a freezing mixture. V. sol. water, alcohol, ether, and benzene. Its nitrosamine is a yellow oil.

α-Amido-iso-valeric acid
$(CH_3)_2CH.CH(NH_2).CO_2H$.

Formation.—1. From NH_3 and α-bromo-iso-valeric acid (Cahours, *A. Suppl.* 2, 83; Fittig a. Clark, *A.* 139, 199; Schmidt a. Sachtleben, *A.* 193, 105) or α-chloro-iso-valeric acid (Schlebusch, *A.* 141, 326).—2. From its nitrile (Lipp, *A.* 205, 18; *B.* 13, 905).

Properties.—Colourless laminæ, composed of minute monoclinic prisms; v. sol. water, v. sl. sol. cold alcohol or ether. Neutral. May be sublimed.

Salts. — HA'HCl: large tables, not deliquescent in moist air. — $HA'HNO_3$. — CuA'_2: scales, sl. sol. hot water. — AgA': spherical groups of crystals, v. sl. sol. water.

Amide $Me_2CH.CH(NH_2).CO.NH_2$. The hydrochloride, got by action of fuming HCl on the nitrile, forms monoclinic plates, v. sol. water. —$(B'HCl)_2PtCl_4$: prisms.

Nitrile $Me_2CH.CH(NH_2).CN$. From isobutyric aldehyde-ammonia and HCN (L.). Yellow oil; m. sol. water, v. sol. alcohol and ether; gradually changes to imido-di-valeronitrile, $NH(CHPr.CN)_2$, giving off NH_3. **Salts.**—B'HCl: insol. ether.—$(B'HCl)_2PtCl_4$.

β-Amido-*iso*-valeric acid
$(CH_3)_2C(NH_2).CH_2.CO_2H$aq [c. 215°].

Formation.—1. Among the products of oxidation of the sulphate of diacetonamine (Heintz, *A.* 198, 51).—2. By reduction of β-nitro-iso-valeric acid (Bredt, *B.* 15, 2321).

Properties.—Crystalline powder; begins to sublime at 180°. V. e. sol. water, sl. sol. alcohol, insol. ether.

Salts.—HA'HClaq: needles, [c. 120°].—$(HA'HCl)_2PtCl_4$.—$CuA'_2$2aq: large crystals.—AgA'.—$(AgA')_2AgNO_3$aq.

Amido-valeric acid $C_5H_9(NH_2)O_2$. Found in the radicles of the sprouting lupin seeds. It occurs along with amido-phenyl-propionic acid, from which it may be separated by virtue of the greater solubility of its copper salt (Schulze a. Barbieri, *J. pr.* [2] 27, 352).

Properties. — Glittering plates, resembling leucine (from alcohol). When heated, a woolly substance sublimes out of it. Gives no pp. with cupric hydrate or acetate (difference from leucine). **Salt.**—HA'HCl: deliquescent prisms.

Constitution. — Probably identical with Lipp's α-amido-*n*-valeric acid (*A.* 211, 354).

Amido-valeric acid. Occurs in the pancreas of oxen (Gorup-Besanez, *A.* 98, 15). Prisms; v. sl. sol. alcohol (difference from leucine). The hydrochloride forms slender deliquescent needles. An amido-valeric acid was found by Schützenberger (*A. Ch.* [5] 16, 283) among the products of the decomposition of albumen by baryta-water.

AMIDO-VERATRIC ACID *v. di-methyl-di-oxy-amido-benzoic acid.*

AMIDOXIMS. *Oxy-amidines. Oxy-imid-gamides.* The oxims of amides, the general formula being R.C(NOH).NH_2.

Formation.—1. By action of hydroxylamine upon nitriles: $R.CN + N(OH)H_2 = R.C(NOH).NH_2$. 2. By heating the thio-amides with alcoholic solution of hydroxylamine (Tiemann, *B.* 19, 1668): $R.CS.NH_2 + H_2NOH = R.C(NOH).NH_2 + H_2S$.

Properties.—The amidoxims combine with acids; they also contain hydrogen displaceable by metals. The acid salts of the alkaline metals, $RC(NOK).NH_2$, $RC(NOH).NH_2$ crystallise well. The stability is increased by the presence of electro-negative substituents; thus, nitro-benz-amidoxim can be reduced to amido-benz-amidoxim without destruction of the amidoxim group.

Ethers.—$R.C(NOEt).NH_2$. These are formed by the action of iodide of ethyl (or of other alkyls) upon the alkaline salts, such as $R.C(NOK).NH_2$. They are bases.

Reactions.—1. Split up by treatment with *acids* or *alkalis* into NH_3, hydroxylamine, and the corresponding acid: $R.C(NOH).NH_2 + 2H_2O = R.CO.OH + H_2NOH + NH_3$. This reaction takes place most readily with methenyl-amidoxim (isuretine) and ethenyl-amidoxim, while benzenyl-amidoxim requires long boiling with HCl before it is decomposed. In this saponification of amidoxims the amide seems to be first formed: $R.C(NOH).NH_2 + H_2O = R.CO.NH_2 + H_2NOH$.—2. The hydrochlorides are converted by *sodium nitrite* into amides: $R.C(NOH).NH_2HCl + NaNO_2 = R.CO.NH_2 + NaCl + N_2O + H_2O$.—3. They combine with *phenyl cyanate* forming bodies called uramidoxims; *e.g.*: $Ph.C(NOH).NH_2 + PhNCO = Ph.C(NOH).NH.CO.NHPh$.—4. *Chlorides of acid radicles*, R'.CO.Cl, form alkoyl derivatives, R.C(N.O.CO.R').NH_2, which can split off water forming azoxims $R.C\langle{}^{N.O}_{N}\rangle CR$. These azoxims, although of high boiling point, are extremely volatile in the vapour of other liquids, even ether.—5. *Dibasic organic anhydrides* give rise to carboxylic acids of azoxims, *e.g.*: $R'.C(NOH).NH_2 + R''\langle{}^{CO}_{CO}\rangle O = R'.C\langle{}^{N.O}_{N}\rangle C.R''.CO_2H + H_2O$.—6. *Chloroformic ether* produces bodies of the composition $R.C(NH_2)$:N.O.CO_2Et.—7. *Carbonyl chloride* gives carbonyl-di-oxims, $(R.C(NH_2):N.O)_2CO$.—8. *Chloral* forms crystalline addition-products.

References.—Tiemann, *B.* 18, 1060, 2456;

19, 1475. The Amidoxims are described as FORMAMIDOXIM, ETHENYL-AMIDOXIM, HEXOAMIDOXIM, BENZAMIDOXIM, CINNAMIDOXIM, TOLUAMIDOXIM, BENZAMIDOXIM CARBOXYLIC ACID, NITRO-BENZAMIDOXIM, &c.

AMIDO-XYLENE *v.* XYLIDINE.

Exo-Amido-xylene $CH_3.C_6H_4.CH_2.NH_2$ [1:3?]. (196°). From $CH_3.C_6H_4.CH_2Cl$ and alcoholic NH_3 (Pieper, *A.* 151, 120). Oil. Salts.—B'HCl [185°].—$B'_2H_2PtCl_6$.

Exo-Amido-*p*-xylene $CH_3.C_6H_4.CH_2.NH_2$ [1:4]. From $CH_3.C_6H_4.CS.NH_2$, tin, and HCl (Paterno a. Spica, *B.* 8, 441).

di-Amido-xylene *v.* XYLYLENE DIAMINE.

tri-Amido-xylene $C_8H_{13}N_3$ *i.e.* $C_6HMe_2(NH_2)_3$ [1:3:4:6:2]. Formed by reducing tri-nitro-*m*-xylene [177°] (Greving, *B.* 17, 2427). White needles which may be sublimed.

AMIDO-XYLENE-SULPHONIC ACID $C_8H_{11}NSO_3$.

Amido-xylene sulphonic acid $C_6H_2(NH_2)Me_2SO_3H$ [4:1:3:6]. S. ·276 at 0°; ·735 at 100°. From (1,3,4)-xylidine and H_2SO_4 or from nitro-*m*-xylene sulphonic acid (Jacobsen a. Ledderboge, *B.* 16, 193). Salts.—NaA'aq and KA'aq form large trimetric tables.—BaA'_2aq: minute needles, v. sol. water.—BaA'_22aq (Sartig, *A.* 230, 334; Nölting a. Kohn, *B.* 19, 137). Diazo compound $C_8H_2Me_2N_2SO_3$: plates.

Amido-*p*-xylene sulphonic acid $C_6H_2Me_2(NH_2)(SO_3H)$ [1:4:6:2]. From *p*-xylene sulphonic acid by nitration and reduction (Nölting a. Kohn, *B.* 19, 143). Needles (with aq): sl. sol. cold water. Its salts are easily soluble. Does not give xyloquinone on oxidation.

Amido-*p*-xylene sulphonic acid $C_6H_2Me_2(NH_2)SO_3H$ [1:4:2:5]. From amido-*p*-xylene and fuming H_2SO_4 or by heating its acid sulphate at 230°. Readily oxidised by CrO_3 to xyloquinone. Salts.—NaA': plates, v. sol. water.—BaA'_27aq (Nölting, *B.* 18, 2664; 19, 141).

Di-amido-xylene sulphonic acid $C_6HMe_2(NH_2)_2SO_3H$ [1:3:6:?:4]. From nitro-xylidine sulphonic acid and ammonium sulphide (Limpricht, *B.* 18, 2190; Sartig, *A.* 230, 343). Fawn-coloured prisms, sl. sol. water, insol. alcohol. Fe_2Cl_6 colours the solution wine-red. Salts: $BaA'_23\frac{1}{2}aq$.—KA'aq.—PbA'_2.—HA'HClaq.

AMIDO-*m*-XYLENOL $C_8H_{11}NO$ *i.e.* $C_6H_2Me_2(NH_2)(OH)$ [1:3:*x*:*y*]. [161°]. Got by reducing nitro-xylenol (Pfaff, *B.* 16, 1137). White glistening crystals. Salt: B'HCl: plates.

Amido-*p*-xylenol $C_6H_2(CH_3)_2(NH_2)(OH)$ [1:4:3:6]. [242°]. White scales. Formed by reduction of nitroso-*p*-xylenol (phlorone-oxim) with tin and HCl (Goldschmidt a. Schmid, *B.* 18, 570; Sutkowski, *B.* 20, 979). CrO_3 oxidises it nearly quantitatively to phlorone.

Salt: B'HCl: white crystals.

AMINES. An amine is a body obtained by displacing hydrogen in ammonia by one or more alcohol radicles. They may be divided into mono-, di-, tri-, and tetra- amines according as it is considered that their molecule is derived from one, two, three, or four molecules of ammonia. Monamines are spoken of as primary, secondary, or tertiary, according as one, two, or three of the atoms of hydrogen in the molecule of ammonia is held to have been displaced by one or more alkyls. If part of the hydrogen has been displaced by an acid radicle (alkoyl) and part by an alcoholic radicle (alkyl) the product may be viewed either as an amide or as an amine, thus NMeAcH may be called methyl-acetamide or acetyl-methylamine. In this dictionary the latter name will be used, such derivatives being described under the amines from which they may be held to be derived. Fatty amines are amines in which the nitrogen is attached to carbon that does not form part of a ring; aromatic amines are bases in which the nitrogen is attached to carbon in a benzene nucleus. In addition to these there are amines, such as pyridine and quinoline, in which the nitrogen itself forms part of a ring, and also others in which the nitrogen is united to carbon in rings other than that peculiar to benzene.

Formation.—1. By the action of ammonia on the ethers of inorganic acids. The iodides, bromides, and chlorides of fatty, but not of aromatic, alkyls, combine with ammonia and with the amines (Hofmann, *T.* 1850, i. 93; 1851, ii. 357):

$$NH_3 + EtI = NEtH_3I$$
$$NEtH_2 + EtI = NEt_2H_2I$$
$$NEt_2H + EtI = NEt_3HI$$
$$NEt_3 + EtI = NEt_4I.$$

The fatty alkyl iodides also act upon the hydriodides of the amines, in presence of ammonia:

$$NH_3 + NEtH_3I + EtI = NEt_2H_2I + NH_4I$$
$$NH_3 + NEt_2H_2I + EtI = NEt_3HI + NH_4I$$
$$NH_3 + NEt_3HI + EtI = NEt_4I + NH_4I.$$

It is therefore impossible to prepare a pure base by this method; methyl iodide gives chiefly NMe_4I, while ethyl iodide gives chiefly $NEtH_3I$, but in the case of primary iodides, whatever proportions are taken, the entire series of salts is formed. Isobutyl iodide does not form the quaternary iodide, secondary butyl iodide forms hardly any tri-butylamine, but only mono- and di-butylamine, while tertiary butyl iodide is split up by NH_3 into isobutylene and HI. NEt_3 at 100° splits up isopropyl iodide and tertiary butyl iodide forming NEt_3HI and olefine (Hofmann, *B.* 7, 513; Reboul, *C. R.* 93, 69). Secondary propyl, hexyl, and octyl iodides form only mono-amines when heated with ammonia (Jahn, *M.* 3, 165). In the action of alkyl chlorides upon aqueous NH_3, the higher the molecular weight, the less primary amine is formed (Malbot, *C. R.* 104, 998).

Ammonium iodide can be separated by its insolubility in alcohol. The compounds NR_3HI, NR_2H_2I, and NRH_3I are decomposed by KOHAq with formation of KI and NR_3, NR_2H, or NRH_2 respectively, while tetra-alkylated ammonium iodides are not affected. The following method may be employed in the preparation of fatty amines (Hofmann, *B.* 3, 776). The alkyl iodide, RI, is heated with alcoholic NH_3 at 100°; the product is filtered from NH_4I, evaporated, and distilled with potash. NR_4I remains behind. The distillate, dried by means of solid KOH, is cooled and treated with oxalic ether which is slowly added. The following reactions then occur:

$$EtO.CO.CO.OEt + 2NRH_2 = HRN.CO.CO.NRH + 2HOEt$$
$$EtO.CO.CO.OEt + NR_2H = EtO.CO.CO.NR_2 + HOEt.$$

The reaction is completed by heat, and the

tertiary base, NR_3, which does not react with oxalic ether, is distilled off. The residue is well cooled and the solid di-alkyl oxamide separated from the liquid di-alkyl-oxamic ether by pressure. The latter is purified by washing with water. Boiling potash liberates the alkylamine from the di-alkyl oxamide and the di-alkyl-amine from the di-alkyl-oxamic ether.

When the halogen is situated in a benzene nucleus ammonia cannot effect its displacement by amidogen unless other chlorous groups are also present in the nucleus. Thus *o*- and *p*-chloro-nitro-benzene (but not *m*-chloro-nitro-benzene) are converted into nitro-anilines by alcoholic NH_3 at 100°.

Primary monamines may be prepared by acting with KOH on the alkyl ammonium sulphates (Morrison, *Pr. E.* 28, 693):

$MeNH_3SO_4 + 2KOH = K_2SO_4 + MeNH_2 + 2H_2O$.

2. By boiling alkyl cyanates with potash (Wurtz, *C. R.* 28, 223), thus: $EtNCO + H_2O = EtNH_2 + CO_2$. The primary bases prepared by this reaction may be contaminated with secondary and tertiary bases. This occurs when the potassic cyanate used to prepare the alkyl cyanates contains cyanide (Silva, *C. R.* 64, 299).

3. Similarly, from thiocarbimides and H_2SO_4: $EtNCS + H_2O = EtNH_2 + COS$.

4. By the reduction of nitro compounds: $RNO_2 + 3H_2 = RNH_2 + 2H_2O$. This reaction is chiefly used in the aromatic series, inasmuch as it is easy to prepare nitro derivatives of compounds containing a benzene nucleus.

The following reducing agents may be used:

(*a*.) Alcoholic *ammonium sulphide*. The compound is dissolved in alcohol, saturated with NH_3 and H_2S is then passed in. The solution is boiled, filtered from S, acidified, and evaporated; a salt of the base is then left: $C_6H_5NO_2 + 3H_2S = C_6H_5NH_2 + 2H_2O + S_3$ (Zinin, *A.* 44, 283). This method is especially useful in reducing nitro-azo compounds which would give hydrazo compounds if reduced in acid solution.

Substances containing several nitroxyls usually have only one of them reduced when treated in this way.

(*b*.) *Zinc dust* may be used either alone, by mixing the substance with it and distilling, or it may be used in conjunction with water or aqueous potash: $Zn + 2KOH = K_2ZnO_2 + H_2$.

(*c*.) *Ferrous sulphate and aqueous ammonia* are used in reducing unsaturated and unstable compounds.

(*d*.) *Arsenious acid* and NaOHAq.

(*e*.) *An acid and a metal.* For the acid, HClAq or HOAc is used; for the metal, zinc, tin, or iron, is taken. Tin and HClAq give, as a rule, the best results. A mixture of zinc and tin is as effective as pure tin, for the zinc pps. the tin as fast as it dissolves. The amount of acid used may sometimes be very small; thus, in the preparation of aniline, the action seems to be:

$4C_6H_5NO_2 + 4H_2O + 9Fe = 4C_6H_5NH_2 + 3Fe_3O_4$.

(*f*.) *Stannous Chloride.* In reducing with $SnCl_2$ and HCl the resulting $SnCl_4$ sometimes chlorinates the product; thus *o*-nitro-toluene gives chloro-*o*-toluidine. The nitroxyls of poly-nitro derivatives may be reduced one by one by adding to their cold alcoholic solution the calculated quantity of $SnCl_2$ dissolved in alcohol saturated with HCl. In the case of dinitro-toluene $C_6H_3Me(NO_2)_2$ [1:2:4] the nitroxyl in the *o* position is first reduced, forming $C_6H_3Me(NH_2)(NO_2)$ [1:2:4]; whilst alcoholic ammonium sulphide reduces the nitroxyl in the *p* position, forming $C_6H_3Me(NO_2)(NH_2)$ [1:2:4] (Anschütz a. Heusler, *B.* 19, 2161).

(*g*.) *Hydric iodide solution*, alone, or with addition of phosphorus.

5. By the reduction of nitriles (Mendius, *A.* 121, 229): $CH_3CN + 2H_2 = CH_3.CH_2.NH_2$.

The reduction is effected by Zn and dilute H_2SO_4 but it is slow, and a great deal of nitrile is saponified: $CH_3.CN + 2H_2O = CH_3.CO_2NH_4$.

6. Primary bases are instantly formed when carbamines are treated with acids:

$CH_3NC + 2H_2O = CH_3NH_2 + HCO_2H$.

7. By boiling bromo-amides with aqueous NaOH. If bromine and potash be simultaneously supplied to an amide, a potassium bromo-amide, X.CO.NKBr, is formed. If this compound be treated with silver carbonate, an alkyl cyanate is produced: X.CO.NKBr = KBr + X.N.CO.

When this cyanate is boiled with potash an alkylamine is formed (by *Formation* 2). The two last stages may be performed simultaneously by boiling the potassium bromo-amide with aqueous NaOH.

The operation is conducted as follows:

Bromine is mixed with its equivalent of amide, and a 10 p.c. solution of potash is added till the colour of the bromine has nearly disappeared.

$$X.CO.NH_2 + Br_2 + 2KHO = X.CO.NKBr + KBr + 2H_2O.$$

Three equivalents of potash dissolved so as to form a 30 p.c. solution are now heated to 70° in a retort, and the first solution is added gradually through the tubulus. Finally the whole is distilled, and the base collected in a receiver containing hydric chloride. A mixture of ammonium chloride and the hydro-chloride of the base is thus got; they may be separated by alcohol, which does not dissolve the former (Hofmann, *B.* 15, 765).

8. Amides can be converted into amines by heating with alcohols: thus acetamide and ethyl alcohol give ethylamine acetate $CH_3.CO.NH_2 + HOEt = CH_3.CO.ONEtH_3$, while ethyl-acetamide and ethyl alcohol give diethyl-amine acetate (Baubigny, *C. R.* 95, 646).

$CH_3.CO.NEtH + HOEt = CH_3CO.ONEt_2H_2$.

Sodium alcoholates act similarly (Seifert, *B.* 18, 1355):

X.NH.CO.Y + NaOR = X.NH.R + NaO.CO.Y.

9. From amido-acids by heating alone or with baryta: $C_6H_4(NH_2)CO_2H = C_6H_5NH_2 + CO_2$.

10. From alcohols or phenols by displacing hydroxyl by amidogen. Ethyl and methyl alcohols give a little ethyl- and methyl-amine when heated with NH_4Cl at 300° (Weith, *B.* 8, 459). Similarly, phenols produce small quantities of amines when heated with NH_3; this reaction takes place very readily in the naphthalene and anthracene series. *Ortho*- and *para*-, but not *meta*-, nitro-phenols are converted by aqueous ammonia into nitranilines (Merz a. Ris, *B.* 19, 1749). The reaction takes place more readily when the alcohols are heated at 260° with the compound $ZnCl_2NH_3$ or $CaCl_2NH_3$ (Merz a. Weith, *B.* 13, 1300; 14, 2343; Merz a.

Gasiorowski, *B.* 17, 628; Merz a. Buch, *B.* 17, 2634). **Ammonia-zinc-chloride converts phenol into aniline; aniline-zinc-chloride acting upon phenol gives di-phenylamine.** β-naphthol is converted by heating with NH_3 into naphthyl-amine, but by ammonia-zinc-chloride into di-β-naphthyl-amine. Fatty alcohols act differently upon aromatic bases in presence of $ZnCl_2$, the alkyl entering the nucleus; thus aniline-zinc-chloride and alcohol produce amido-phenyl-ethane:

$$C_6H_5NH_2 + HOEt = C_6H_4EtNH_2 + H_2O.$$

11. By reduction of the phenyl-hydrazides of the aldehydes and ketones in alcoholic solution by sodium-amalgam and acetic acid (Tafel, *B.* 19, 1924):

$$RR'C:N_2HPh + 2H_2 = RR'CH.NH_2 + PhNH_2.$$

12. By reduction of aldoxims and ketoxims in alcoholic solution by sodium amalgam and acetic acid (Goldschmidt, *B.* 19, 3232):

$$RR'C:NOH + 2H_2 = RR'CH.NH_2 + H_2O.$$

13. From sulphonates by heating with sod-amide (Jackson a. Wing, *B.* 19, 902):

$$R.SO_3K + NaNH_2 = R.NH_2 + NaKSO_3.$$

Properties.—Most amines are volatile or can be distilled alone or with the aid of steam. Primary bases in which amidogen is not united to carbon in a benzene nucleus turn red litmus paper blue and combine with carbonic acid; aniline and its homologues are neutral to litmus, and do not combine with carbonic acid. Ammonia pps. the amines from cold aqueous solutions of their salts; but at high temperatures the amines expel NH_3 from its salts. The relative saponifying power of amines has been studied by Ostwald (*J. pr.* [2] 35, 112). If a mixture of aromatic bases is dissolved in an excess of glacial acetic acid, and the solution is diluted with three times its volume of water and then boiled, the primary amines remain in solution while the acetates of secondary and tertiary amines are decomposed and the bases are found on the filter (Michael, *B.* 19, 1391). To determine whether a given base is primary, secondary, or tertiary, it is heated with methyl iodide until a quaternary iodide is formed; this iodide is known by its stability towards potash. The original base and the ammonium iodide are both analysed. If the ammonium iodide differs in composition by containing CH_3I more than the base, then the base was tertiary. If it differ by C_2H_5I, this shows that the original base was secondary, and had to exchange hydrogen for methyl before it could become tertiary. If the iodide contains C_3H_7I more than the base, then the latter was primary.

Reactions 1, 2, 3, 4, 5, 6, 11, 12, 15, 20, 27, 28, may also be used to distinguish between primary, secondary, and tertiary bases.

When a quaternary ammonium base is distilled, if it contains ethyl it splits up thus:

$$NRR'R''C_2H_5(OH) = NRR'R'' + C_2H_4 + H_2O;$$

(Hofmann, *B.* 14, 494).

Quaternary ammonium chlorides containing methyl split off MeCl on distillation:

$$NRR'R''MeCl = NRR'R'' + MeCl;$$

(Lossen, *A.* 181, 377).

Reactions 3, 5, 6, 12, 13, 26, and 28, serve to distinguish *o*-diamines from *m*- and *p*- diamines.

Reactions.—1. If a primary base be boiled with ***alcoholic potash*** and ***chloroform*** the disgusting odour of the corresponding carbamine will be noticed (Hofmann, *B.* 3, 767):

$$EtNH_2 + CHCl_3 + 3KHO = EtNC + 3KCl + 3H_2O.$$

2. If a primary fatty base be dissolved in alcohol mixed with an equal volume of CS_2, and the liquid be boiled down to half its volume, a thiocarbamate will be formed:

$$2RNH_2 + CS_2 = RNH.CS.S.NRH_3.$$

If the liquid be now boiled with a little aqueous mercuric or ferric chloride a pungent odour of an alkyl mustard oil (or thiocarbimide) will be perceived, thus: $RNH.CS.SNRH_3 + HgCl_2 = HgS + RNCS + NRH_3Cl + HCl$. In the aromatic series the product of the action of alcoholic CS_2 is usually a thio-urea which requires to be treated with P_2O_5 in order to get the thiocarbimide (Hofmann, *B.* 3, 768; 8, 107; Weith, *B.* 8, 461). Mesidine and amido-penta-methyl-benzene give thio-carbimides in addition to smaller quantities of the thio-ureas (Hofmann, *B.* 18, 1827).—3. *Nitrous acid* converts primary fatty amines into alcohols: $RNH_2 + HNO_2 = ROH + N_2 + H_2O$. It converts primary aromatic amines into diazo-compounds: $RNH_2 + HNO_2 = RN_2OH + H_2O$. It converts all secondary bases into nitrosamines, which are neutral substances, volatile with steam: $RR'NH + HNO_2 = RR'N.NO + H_2O$. It cannot act upon tertiary fatty bases, except with elimination of an alkyl. It converts most tertiary aromatic bases into nitroso derivatives, which still possess basic properties:

$$C_6H_5NMe_2 + HNO_2 = C_6H_4(NO)NMe_2 + H_2O.$$

Aromatic nitrosamines are converted into *p*-nitroso derivatives under the influence of acids. $C_6H_5NMe(NO) = C_6H_4(NO).NMeH$. By means of the preceding reactions, nitrous acid may be used to separate secondary from primary and tertiary bases, for the nitrosamines do not combine with acids, and may therefore be extracted from the acid solution by ether, or by distilling with steam: and on reduction they give the secondary base. If the diazo compounds are boiled with water phenols are formed: $RN_2Cl + H_2O = ROH + N_2 + HCl$, while if they are boiled with alcohol, the amidogen is usually displaced by hydrogen: $RN_2Cl + C_2H_6O = RH + HCl + C_2H_4O$. Frequently, however, boiling with alcohol displaces amidogen by ethoxyl: $C_6Me_4H.N_2Cl + HOEt = C_6Me_4H.OEt + HCl + N_2$ (Hofmann, *B.* 17, 1917). Amidogen may also be displaced by hydrogen by reducing the diazo compound to a hydrazine and boiling the latter with aqueous $CuSO_4$ (Haller, *B.* 18, 90). In order to displace amidogen by chlorine we may distil the platinochloride of the diazo derivative; to displace amidogen by bromine we may boil the perbromide of the diazo derivative with alcohol; to displace it by iodine we may boil the diazo salt with aqueous HI or KI. These operations may be more conveniently performed by the method of Sandmeyer (*B.* 17, 1633, 2650). This method consists in boiling the diazo compounds with cuprous chloride, bromide, iodide, or cyanide.

Examples.—(*a*) 4 g. *m*-nitro-aniline, 7 g. HCl (S.G. 1·17), 100 g. water, and 20 g. of a 10 p.c. solution of cuprous chloride in HClAq are heated to near boiling and 2·5 g. sodic nitrite dissolved in 20 g. water are slowly added, the mixture being well shaken. 4 g. pure *m*-chloro-nitro-benzene is obtained.

(*b*) 12·5 g. crystallised cupric sulphate, 36 g. KBr, 80 g water, 11 g. H_2SO_4 (S.G. 1·8), and 20 g. copper turnings are boiled until the dark colour has nearly disappeared. Aniline (9·3 g.) is now added, and the boiling liquid treated as before with $NaNO_2$ (7 g.) dissolved in water (40 g.). Bromo-benzene passes over on subsequent distillation.

(*c*.) 25 g. crystallised $CuSO_4$, 150 g. water and 28 g. KCN (96 p.c.) are dissolved in hot water. A solution of diazobenzene chloride is run in, this is prepared from 7 g. $NaNO_2$ dissolved in 20 g. water added to a solution of 9·3 g. aniline in 20·6 g. HCl (S.G. 1·17) and 80 g. water. The yield of benzonitrile is 63 p.c. of the theoretical.

In these reactions a double compound between the cuprous salt and the diazo salt is perhaps an intermediate body. Such a double compound has been isolated in the case of β-naphthylamine, $C_{10}H_7N_2BrCu_2Br_2$ (Lellmann a. Remy, *B.* 19, 810). Substitution of amidogen by halogens may also be effected by gradually adding HNO_3 to a hot solution of the amine in HCl, HBr, or HI (Losanitsch, *B.* 18, 39).

Amidogen may be changed into SH by heating the diazotised base with warm alcoholic potassium sulphide. By oxidising the resulting mercaptan with $KMnO_4$ a sulphonic acid is got (Klason, *B.* 20, 349).

Nitrous acid serves to distinguish *o*-, *m*-, and *p*- diamines (*v.* di-Azo-compounds).

4. *Benzoyl chloride* acts on primary and secondary amines:

$$RNH_2 + BzCl = RNBzH + HCl,$$
$$RR'NH + BzCl = RR'NBz + HCl$$

(Hofmann, *B.* 5, 716; Hallmann, *B.* 9, 846). Tertiary aromatic amines heated with it at 200° may exchange alkyl for benzoyl:

$$NPhEt_2 + BzCl = NPhEtBz + EtCl$$

(Hess, *B.* 18, 685).

5. *Acetyl chloride* converts primary and secondary amines into acetyl derivatives.

The di-alkylated tertiary aromatic amines readily allow one of the alkyl groups to be replaced by acetyl when treated with acetyl *bromide*, the alkyl bromide formed converting another portion into quaternary ammonium bromide: $2XNR_2 + AcBr = XNRAc + XNR_3Br$.

The reaction sets in spontaneously, and is completed on gentle warming (Staedel, *B.* 19, 1947).

Primary aromatic amines may be converted into acetyl derivatives by boiling not only with AcCl or Ac_2O but even with glacial HOAc.

The alkoyl derivatives of *o* but not of *m* and *p* aromatic diamines give rise to anhydro compounds:

$$C_6H_4{<}^{NH.CO.CH_3}_{NH_2} = H_2O + C_6H_4{<}^{NH}_{N}{>}C.CH_3$$

(Hübner, *A.* 208, 278).

6. *Aldehydes* form products of condensation with amines. Œnanthol is recommended by Schiff (*A.* 159, 158) as a means of distinguishing between the different classes of amines. Primary amines require one equivalent of œnanthol:

$$C_7H_{14}O + PhNH_2 = PhN(C_7H_{14}) + H_2O,$$

while secondary amines require only half as much aldehyde:

$$C_7H_{14}O + 2Me_2NH = (Me_2N)_2(C_7H_{14}) + H_2O.$$

The base is dissolved in benzene and a standard solution of œnanthol in benzene is run in as long as it produces further separation of drops of water.

Tertiary aromatic amines can also condense with aldehydes: $2PhNEt_2 +$ [1:2] $C_6H_4(NO_2).CHO = NO_2.C_6H_4.CH(C_6H_4NEt_2)_2 + H_2O$. Aromatic amines heated with aldehydes and $ZnCl_2$ give tri-substituted methanes (Fischer, *B.* 15, 676).

In order to distinguish whether an aromatic diamine is an *ortho* compound, Ladenburg (*B.* 11, 600) heats its hydrochloride with benzoic aldehyde; if the compound is *ortho* an aldehydine (*q. v.*) is formed and HCl is evolved, while no HCl is evolved in the case of *m* or *p* compounds.

$$R''(NH_2HCl)_2 + 2PhCHO =$$
$$R''(N_2C_2H_2Ph_2)HCl + 2H_2O + HCl.$$

7. *Bromine and aqueous potash* convert primary amines into di-bromamines:
$MeNH_2 + 2Br_2 + 2KOH = MeNBr_2 + 2KBr + 2H_2O$. Secondary amines, containing one divalent alkyl, behave similarly:
$C_8H_{14}NH + Br_2 + KOH = C_8H_{14}NBr + KBr + H_2O$
but secondary amines containing two monovalent alkyls are split up into an alkylene bromide and a primary alkylamine (Hofmann, *B.* 16, 559).

The di-bromo-amines containing hexyl and its higher homologues are split up by aqueous NaOH into HBr and nitriles:

$$C_7H_{15}CH_2NBr_2 + 2NaOH =$$
$$C_7H_{15}CN + 2NaBr + 2H_2O.$$

Hence amides may be converted first into amines and then into nitriles by treatment with bromine and NaOHAq, the first reaction being:

$$C_7H_{15}CH_2.CO.NH_2 + Br_2 + 4NaOH =$$
$$C_7H_{15}CH_2.NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

(Hofmann, *B.* 17, 1920).

8. *Sulphuric oxide* combines with primary and secondary fatty amines, forming small quantities of sulphamic acids:

$$NEt_2H + SO_3 = NEt_2.SO_3H.$$

It also combines with tertiary fatty amines:

$NEt_3 + SO_3 = Et_3N{<}^{SO_2}_{O}{>}$ (Beilstein a. Wiegand, *B.* 16, 1264).

It combines with aromatic amines forming sulphonic acids:

$$C_6H_5NH_2 + SO_3 = C_6H_4(SO_3H)NH_2.$$

Aromatic amines may also be sulphonated by H_2SO_4 and by $ClSO_3H$.

9. *Sulphuryl chloride* acts upon secondary fatty amines thus, forming tetra-alkyl sulphamides: $SO_2Cl_2 + 2HNEt_2 = SO_2(NEt_2)_2 + 2HCl$. With the hydrochlorides of these bases the reaction stops half way: $SO_2Cl_2 + HCl.NHEt_2 = Cl.SO_2.NEt_2 + 2HCl$ (R. Behrend, *A.* 222, 116).

10. *Zinc ethide* does not attack tertiary amines, but acts upon primary and secondary amines in the following ways:

$$2RNH_2 + ZnEt_2 = R_2N_2H_2Zn + 2HEt,$$
$$2RR'NH + ZnEt_2 = R_2R'_2N_2Zn + 2HEt$$

(Frankland, *Pr.* 8, 504; Gal, *C. R.* 96, 578).

11. *Cyanic ethers* unite with primary and secondary bases forming alkyl-ureas:

$$RNH_2 + R'NCO = RNH.CO.NR'H,$$
$$RR''NH + R'NCO = RR''N.CO.NR'H.$$

Cyanic acid acts similarly:

$$RNH_2HCl + KNCO = RHN.CO.NH_2 + KCl$$

12. *Thio-carbimides* unite with primary and secondary amines forming thio-ureas:

$$RNH_2 + R'NCS = RNH.CS.NR'H.$$

When the solid product obtained by boiling an

aromatic di-amine with alcohol and oil of mustard (C_3H_5NCS) is gradually heated, then if the diamine were *o* it would solidify above its melting-point; if it were *m* it would melt without further change and would therefore solidify on cooling; if it were *p* it would melt and undergo decomposition and on cooling would remain liquid (Lellmann, *A.* 221, 1; 228, 248; *B.* 19, 808). In all cases di-thio-ureas, $R''(NH.CS.NHC_3H_5)_2$, are first formed; those from *m*-diamines are not affected by heat, while the *o* and *p* derivatives split up on melting thus:

$$R''(NH.CS.NHC_3H_5)_2 =$$
$$R''<{NH \atop NH}>CS + CS(NHC_3H_5)_2.$$

13. The *di-sulphocyanides* of the *o*-diamines are changed at 120°–130° into thio-ureas, $C_xH_y<{NH \atop NH}>CS$, which are not desulphurised by hot solution of PbO in NaOHAq. The *m* and *p* diamines give compounds of the form $C_xH_y(NH.CS.NH_2)_2$ which are desulphurised by this reagent (Lellmann, *A.* 228, 8, 248).

14. Small quantities of orthodiamines are readily detected by adding a few drops of a hot acetic acid solution of *phenanthraquinone* to an alcoholic solution of the substance; if an orthodiamine is present a yellow crystalline pp. of the corresponding quinoxaline is formed on boiling the solution; this pp. in the case of phenylene and tolylene *o*-diamines is coloured deepred by HCl (Hinsberg, *B.* 18, 1228).

15. If a mixture of bases is treated with sufficient *citraconic acid* to form the acid salts and the aqueous solution is boiled the primary amines will be ppd. in the form of alkyl-citraconamic acids, while the secondary and tertiary amines can be obtained by distilling the filtrate with steam (Michael, *B.* 19, 1390).

16. *Oxidising agents* convert aromatic amines into azo or azoxy compounds. Hence the nitration of such amines by the usual methods requires previous introduction of acetyl into the amidogen. But by treating the nitrates with cold conc. H_2SO_4 nitro-amines may be prepared, the nitroxyl taking a *m* position with regard to amidogen (Levinstein, *D. P. J.* 256, 471).

17. Amines form condensation products with *quinones*, *e.g.*

$$C_6H_2O_2(NHPh)_2;\ C_6H_2O(NPh)(NHPh)_2.$$

18. Aromatic amines when boiled with *fatty amides* produce ammonia and alkyl-amides, *e.g.* $CH_3.CO.NH_2 + NPhH_2 = CH_3.CO.NPhH + NH_3$.

19. *Silver salts* form additive compounds with amines (Mixter, *A. C. J.* 1, 239).

20. The *ferrocyanides* are obtained by adding the amines to a mixture of aqueous K_4FeCy_6 and hydrochloric acid; a crystalline pp. of the acid ferrocyanide $B'_2H_4FeCy_6xaq$, is usually formed (Fischer, *A.* 190, 184; Eisenberg, *A.* 205, 265). The ferrocyanides of tertiary amines are particularly insoluble in water and may be used as a means of isolating those amines. To recover the amine, the pp. is suspended in water and decomposed by $CuSO_4$, and the excess of $CuSO_4$ removed from the filtrate by baryta.*

21. *Chloral hydrate* heated with tertiary aromatic amines and $ZnCl_2$ forms a condensation product which, when decomposed by aqueous KOH gives an aldehydo derivative, *e.g.*

$$CCl_3CH(OH)_2 + C_6H_5NMe_2 = CCl_3CH(OH).C_6H_4NMe_2 + H_2O$$
$$CCl_3CH(OH).C_6H_4NMe_2 = CCl_3H + HCO.C_6H_4NMe_2$$

(Boessneck, *B.* 18, 1516; 19, 365).

22. Primary aromatic amines in alcoholic solution absorb *cyanogen*; and the product when boiled with glacial HOAc becomes a di-alkyl-oxamide:

$$2PhNH_2 + C_2N_2 = PhNH.C(NH).C(NH).NPhH$$
$$PhNH.C(NH).C(NH).NPhH + 2H_2O = PhNH.CO.CO.NPhH + 2NH_3.$$

Aromatic *o*-diamines act similarly; the resulting oxalyl-*o*-diamine may be viewed as a di-oxyquinoxaline (Bladin, *Bl.* [2] 42, 104).

23. Primary aromatic amines heated with *glycerin* (or acroleïn), H_2SO_4, and nitrobenzene (as oxidising agent) produce bases of the quinoline series. A similar reaction occurs when glycol (or paraldehyde) is substituted for glycerin.

24. *Nitric oxide* passed into an alcoholic solution of tertiary aromatic bases produces azo-compounds of the form $RR'N.C_6H_4.N_2.C_6H_4.NRR'$.

25. For the action of *aceto-acetic ether*, *v.* p. 19.

26. Orthodiamines form crystalline compounds with *glucose* (Griess a. Harrow, *B.* 20, 281).

27. *Diazobenzene chloride* reacts with primary and with secondary amines, forming diazo-amides (*v.* di-AZO-COMPOUNDS). In the case of the secondary amines the compounds $C_6H_5.N_2.NRR'$, being easily crystallised and sl. sol. water, may be conveniently used in separation of these bases from tertiary and in some cases from primary bases (Wallach, *A.* 235, 235).

28. A solution of *potassium croconate* gives with salts of *o*-diamines dark-coloured pps. consisting of the corresponding azines (Nietzki, *B.* 19, 2727).

29. Tertiary aromatic amines form condensation products when heated with *aromatic acids or alcohols* in presence of $ZnCl_2$ or P_2O_5; water being eliminated at expense of H *para* to N (Fischer, *A.* 206, 85).

OTHER REACTIONS of the amines are described in articles on the several bases, *e.g.* METHYLAMINE, ETHYLAMINE, ANILINE, PHENYLENE-DIAMINE. See also AMIDES, AMIDO ACIDS, AMIDINES, and AMIDOXIMS.

AMISATIN *v.* ISATIN.

AMMELIDE $C_3H_4N_4O_2$ or $C_6H_9N_9O_4$ *i.e.* $C_3N_3(NH_2)(OH)_2$ (?). *Melanurenic acid.* '*Amido-cyanuric acid.*' *Mono-amide of cyanuric acid.* Liebig made a distinction between ammelide and melanurenic acid, but his ammelide was a mixture of ammeline and his melanurenic acid, hence it seems best to transfer the name ammelide to melanurenic acid (Klason, *J. pr.* [2] 33, 295).

Formation. — 1. From melam and conc. H_2SO_4 (Liebig, *A.* 10, 30; Gabriel, *B.* 8, 1165; Jager, *B.* 9, 1554).—2. From melam and boiling conc. KOHAq or conc. H_2SO_4 at 150° (K.).—3. From ammeline and conc. H_2SO_4 at 160° or by heating ammeline nitrate (Knapp, *A.* 21, 244); the change is incomplete.—4. A product of the dry distillation of urea (Liebig a. Wöhler, *A.* 54, 371; Laurent a. Gerhardt, *A. Ch.* [2] 19, 93; Drechsel, *J. pr.* [2] 11, 289).—5. Among products got by boiling mellon-potassium with

aqueous KOH (Hennesberg, *A.* 73, 246; Liebig, *A.* 95, 269).—6. From its ethers or their thio-derivatives by gentle heat (K.).—7. From thio-ammelide and $KMnO_4$ (K.).—8. From cyanogen bromide and cyanamide at 100° (Cech a. Dehmel, *B.* 11, 25).—9. From urea and cyanogen iodide at 150° (Poensgen, *A.* 128, 339; Hallwachs, *A.* 153, 294; Schmidt, *J. pr.* [2] 5, 36).—10. In small quantity by action of $COCl_2$ on NH_3 (Bouchardat, *A.* 154, 355).—11. In small quantity from di-cyan-di-amide by heating with water at 160° or with aqueous ammonic carbonate at 120° (Bamberger, *B.* 16, 1078, 1703).

Preparation.—Conc. H_2SO_4 (300 g.) is slowly poured upon melam (100 g.) and the solution heated for a few minutes to 190°. When cold it is poured into a litre of water, when ammelide sulphate slowly crystallises (Striegler, *J. pr.* [2] 33, 163).

Properties.—White crystalline powder; v. sl. sol. water, insol. usual menstrua, sol. mineral acids, insol. acetic acid, v. sol. ammonia. It does not separate when its solution in warm aqueous NaOH is cooled (difference from ammeline). May be crystallised from boiling water. Not attacked by Cl, Br, HI, or AcCl.

Reactions.—1. Boiling dilute *acids* or *alkalis* form NH_3 and cyanuric acid. *Baryta-water* does not effect this change. — 2. *Phosphorus pentachloride* forms Cy_3Cl_3.—3. $KMnO_4$ in acid solution forms cyanuric acid.—4. *Water* at 170° forms CO_2 and NH_3.—5. Heated in a current of moist CO_2 it forms cyanamide.

Salts.—($H_2A'' = C_6H_8N_8O_4$).—
$H_2A''H_2SO_4$3aq.—H_2A'' 2HNO_3.—H_2A'' 2HCl.—
Na_2A'' 6aq. — $NaHA''$5aq. — K_2A''. — KHA''. —
$(NH_4)_2A''$5aq. — $(NH_4)HA''1\frac{1}{2}$aq. — $CaA''x$aq. —
$BaA''2\frac{1}{2}$aq. — CuA''. — NiA''2aq. — Ag_2A''. —
$AgHA''1\frac{1}{2}$aq (Striegler; Volhard, *B.* 7, 92).

Di-methyl ether $C_5H_8N_4O_2$ *i.e.* $C_3N_3(NH_2)(OMe)_2$. [212°]. Formed by action of ammonia on trimethyl cyanurate, and occurs as a by-product in the preparation of that body (Hofmann a. Olshausen, *B.* 3, 273). Plates, sl. sol. cold alcohol, v. sl. sol. ether, sl. sol. cold water.—$C_5H_8N_4O_2AgNO_3$: needles.

Di-ethyl ether $C_7H_{12}N_4O_2$ *i.e.* $C_3N_3(NH_2)(OEt)_2$. [97°]. By-product in the action of CyCl on NaOEt, and formed by heating cyanetholin with aqueous NH_3 at 100° (H. a. O.). Prisms.—$C_7H_{12}N_4O_2AgNO_3$: needles. —$(C_7H_{12}N_4O_2)_2AgNO_3$: needles.

AMMELINE $C_3H_5N_5O$ *i.e.* $C_3N_3(NH_2)_2(OH)$. '*Di-amido-cyanuric acid.*' *Diamide of cyanuric acid.*

Formation.—1. By boiling melam for a long time with KOHAq or HClAq or by heating it with conc. H_2SO_4 at 100° (Liebig, *A.* 30, 24; Klason, *J. pr.* [2] 33, 286). — 2. From $Cy_3(NH_2)_2Cl$ by alkalis (Lament a. Gerhardt, *A. Ch.* [3] 19, 92).—3. From thio-ammeline and $KMnO_4$.—4. From its ether or its thio derivative by HCl. — 5. Formed by boiling the hydrochloride of 'di-amido-tri-chloro-methyl cyanidine' (*v. Tri*-CHLORO-ACETONITRILE) with NH_3Aq:

$$Cy_3(NH_2)_2(CCl_3)HCl + NH_3 + H_2O =$$
$$Cy_3(NH_2)_2(OH) + NH_4Cl + HCCl_3.$$

Also by heating tri-chloro-acetonitrile with NH_3Aq at 120°, or with alcoholic NH_3 at 170° (Weddige, *J. pr.* [2] 33, 85).

Properties. — Minute needles in dendritic groups (when ppd. from a warm solution). Insol. water, alcohol, ether, and benzene; sol. mineral acids; insol. acetic acid; sol. NH_3Aq. Separates when its solution in warm NaOHAq is cooled.

Reactions.—1. Split up by *heat* into NH_3 and mellon.—2. Warm H_2SO_4 forms NH_3 and ammelide.—3. Boiling dilute *nitric acid* forms first ammelide, then cyanuric acid (Knapp, *A.* 21, 255).

Salts.—Its compounds with acids are decomposed by water.—B'HCl: prisms.—$B'HNO_3$. —$B'AgNO_3$.

Ethyl ether $Cy_3(NH_2)_2OEt$. [190°-200°]. From cyanetholine and NH_3 (Hofmann a. Olshausen, *B.* 3, 275). V. sl. sol. alcohol.

Chloride $Cy_3(NH_2)_2Cl$. '*Chloro-cyanamide.*' From Cy_3Cl_3 and NH_3Aq (Liebig, *A.* 10, 43; Laurent a. Gerhardt, *A. Ch.* [2] 19, 90; 20, 98; Bineau, *A. Ch.* [2] 70, 254). Powder, insol. water. Decomposed by heating with HCl into mellon and NH_3. Dilute KOHAq converts it into ammeline. NH_3 at 100° forms melamine. KHS forms thio-ammeline.

AMMONIA NH_3. (*Volatile Alkali. Alkaline air.*) Mol. w. 17·01. [−75°. Faraday, *Q. J. S.* 19, 16]. (−38·5°; pressure less than 760 mm. Regnault.) S.G. $\frac{0°}{0}$ (liquid) ·6234 (Jolly, *A.* 117, 181: compare also Andreef, *ibid.* 110, 1). V.D. 8·5. S. 0°, 1050; 10°, 813; 15°, 727; 20°, 654; (Bunsen, *Gasometry*, Engl. ed. 169). S. 0°, 1148 (Roscoe a. Dittmar, *A.* 110, 140); S. 0°, 1270 (Berthelot, *C. R.* 76, 1041). C.E. (liquid −11° to 0°) ·00155 (Jolly, *A.* 117, 181). Refractive power (gas) compared with air = 1, 1·309. $[N,H^3] = 11{,}890$; $[N,H^3,Aq] = 20{,}320$; $[NH^3,Aq] = 8{,}430$ (*Th.* 2, 68).

Occurrence.—Ammonia salts occur in the atmosphere and in rain water; in many mineral waters; in sea water; near volcanoes; in many soils; in almost all plants; in the excrements of many animals; among the products of the decay of nitrogenous organic bodies. Free ammonia is not known to occur in nature. Ammonia was distinguished from ammonium carbonate by Black in 1756; Priestley obtained it approximately pure and named it *alkaline air*; Scheele showed it to contain nitrogen; Berthollet demonstrated its composition in 1785. The word ammonia comes from *sal ammoniacum*, the name given in the middle ages to ammonium chloride.

Formation.—1. By the action of the induction spark, or the silent discharge (Donkin, *Pr.* 21, 281), on a mixture of N and H in the ratio $N:H_3$ a small quantity of NH_3 is produced (Morren, *C. R.* 48, 432; Perrot, *C. R.* 49, 204; Chabrier, *C. R.* 75, 484).—2. According to Ramsay a. Young (*C. J.* 45, 93) a trace of NH_3 is formed when a mixture of moist N and H is passed through a red-hot tube containing iron filings; 3. Ammonium nitrite is formed, *a.* when hydrogen is burnt in air (Zöller a. Grete, *B.* 10, 2145; but against this *v.* Wright, *C. N.* 38, 240); *b.* by the action of a strong induction-spark on a mixture of N and H_2O (Thenard, *C. R.* 76, 983; Johnson, *C. N.* 48, 253 a. 264). Ammonium chloride is produced when electric sparks are passed for 8 to 10 hours through a mixture of HCl gas, N, and H, the elements being in the

ratio $N:H_3$ (Deville, *C. R.* 60, 317); or by passing the same gases through a red-hot porcelain tube containing a metal tube cooled by a stream of cold water (Deville, *A.* 135, 104).—4. By the action of a porous body—*e.g.* spongy platinum, pumice, ferric oxide—aided by heat, on a mixture of H with an oxide of nitrogen or HNO_3, NH_3 is produced.—5. By decomposing a compound of H and one of N together, NH_3 is formed: *e.g.* by the action of water on nitride of Si, B, Mg &c., SiO_2, B_2O_3, or MgO is produced, and the N and H combine to form NH_3: again moist NO passed over hot iron filings yields NH_3. 6. By strongly heating easily oxidised bodies—*e.g.* As, Zn, K, &c.—with alkaline oxides, in presence of air.—7. By strongly heating metallic nitrates or nitrites with hydroxides of the alkali or alkaline earth metals and iron filings or zinc.—8. By heating metallic cyanides with steam (*v.* Marguerite and Sourdeval, *D. P. J.* 157, 73 and 316).—9. By heating solutions of nitrates or nitrites with KOHAq and Zn or Fe, or with a Cu-Zn couple. Ammonium sulphate is formed when nitric acid is dropped into a vessel containing Zn and dilute H_2SO_4Aq (Kuhlmann, *A.* 64, 233).—10. By the action of water on chloride, iodide, or phosphide, of nitrogen, or on the amides; in the last cases it is often necessary to use solutions of KOH or NaOH.—11. By the dry distillation of many nitrogenous organic bodies—*e.g.* horn, bones, blood, coal, &c. Ammonia is produced, according to Johnson, when N and H are passed over spongy Pt (*C. J.* 39, 128); but this is denied by Wright (*C. J.* 39, 359), whose experiments seem to prove that the NH_3 obtained by Johnson was the product of the mutual action of a trace of NO (in what was supposed to be pure N) and H, in presence of the spongy Pt (but *v.* also Johnson's pamphlet *Elementary Nitrogen, and on the Synthesis of Ammonia* [Churchill, 1885]).

Preparation.—1. By gently heating a mixture of 1 part chloride or sulphate of ammonium with 2 parts finally powdered slaked lime; the mixture is covered with a layer of lime to absorb water, and the gas is dried by passage through a cylinder containing lime in small pieces.—2. By gently heating a solution of $CaCl_2$ in NH_3Aq previously saturated with NH_3; this mixture may be kept unchanged for long.—3. Pure ammonia is prepared by Stas (*Fr.* 6, 423) by one of the following methods:—(i.) From pure NH_4Cl and KOHAq; 10 litres of a boiling conc. solution of NH_4Cl are mixed with 1 litre HNO_3Aq, S.G. 1·4; the boiling is continued so long as Cl comes off, the NH_4Cl which separates on cooling is dissolved in hot water, and again boiled with $\frac{1}{20}$ volume of HNO_3 till Cl ceases to come off, water is then added, and NH_3 is obtained by decomposing by KOHAq. (ii.) From pure $(NH_4)_2SO_4$ and KOHAq; 2 kilos. of $(NH_4)_2SO_4$ are heated with $1\frac{1}{2}$ kilos. conc. H_2SO_4 to the temperature whereat the sulphate begins to decompose with effervescence, small quantities of nitric acid are then added until the liquid becomes quite colourless; the salt which crystallises on cooling is dissolved in warm water and decomposed by KOHAq. [The object of these treatments is to remove the small quantities of substituted ammonias—NH_2CH_3, $NH_2C_2H_5$ &c.—which are present in ammonium chloride and sulphate.] (iii.) From pure KNO_2 by the action of Zn and Fe in presence of KOHAq: the KNO_2 is prepared by heating 1 kilo KNO_3 with metallic copper, and dissolving out the KNO_2 in water; this solution is digested with 15 litres KOHAq—S.G. 1·25—$3\frac{1}{2}$ kilos. granulated zinc free from carbon (Zn obtained by fusing commercial Zn with 5 p.c. PbO may be used), and $\frac{1}{2}$ kilo. iron wire previously strongly heated in air and then reduced by hydrogen; the liquid is poured off and distilled with gentle ebullition.

Properties.—A colourless, strongly-smelling, gas, which turns red litmus paper blue, and turmeric paper brown. Taste, hot and strongly alkaline; poisonous when breathed; it destroys the mucous membrane. Easily liquefied to a limpid, colourless, highly refractive, liquid; best by heating solid $2AgCl.3NH_3$ in one end of a strong glass tube, closed at both ends, and bent to an obtuse angle, the other end being surrounded by snow and salt (Faraday, *Q. J. S.* 19, 16). The silver compound begins to melt at 38°, it is quite liquid at 90°, begins to boil at 100°, and the change is complete at 112°. Liquefied at −40° to −50°; this may be effected by passing the well-dried gas through a U tube surrounded by a mixture of crystallised $CaCl_2$ and snow, or by liquid SO_2 which is rapidly evaporated by a current of air (Loir and Drion, *J.* 1860. 41). If liquid ammonia is cooled by solid CO_2 and ether *in vacuo* (Faraday), or by rapid evaporation over H_2SO_4 (Loir and Drion), white transparent crystals of solid ammonia are obtained, which melt at −75° (Faraday). Liquid ammonia vaporises in a closed vessel, the vapour-pressures according to Regnault (*J.* 1863. 66) being as follows:—

−30°	866·09	mm.	+40°	11,595·30	mm.
−20	1392·13	„	50	15,158·33	„
−10	2144·62	„	60	19,482·10	„
0	3183·34	„	70	24,675·55	„
+10	4575·03	„	80	30,843·09	„
20	6387·78	„	90	38,109·22	„
30	8700·97	„	100	46,608·24	„

Ammonia gas is very soluble in water (*v.* *Combinations* No. 1), alcohol, and ether; it is largely absorbed by charcoal (*v.* Hunter, *C. J.* [2] 9, 76; 10, 649) and other porous substances; it is absorbed by many saline solutions, the quantity of NH_3 absorbed being, as a rule, the less the more concentrated is the solution (*v.* Raoult, *C. R.* 77, 1078). Ammonia solution is a strongly smelling, caustic, alkaline, liquid; at −40° it forms long needle-shaped crystals; at −49° it solidifies to an inodorous mass; the B.P. and S.G. increase the less is the quantity of NH_3 present. Many metallic oxides insoluble in water are dissolved by NH_3Aq, *e.g.* CuO, Ag_2O, &c.; aqueous NH_3 also dissolves many fats and resins. Ammonia resembles PH_3 in its properties and reactions; it is, however, much more stable and less easily oxidised than that compound; an aqueous solution of NH_3, which doubtless contains NH_4OH, is characterised by the properties expressed by the word *alkali* (*v.* Ammonium Compounds; comp. also the arts. Hydrides, Hydroxides, and Nitrogen Group of Elements.)

Reactions.—I. Liquid ammonia does not react with H_2SO_4 at −65°; dissolves alkali metals

at first with red, then blue, colour; the metals crystallise out unchanged (Gore, *Pr.* 21, 140); alkaline earth metals and heavy metals do not dissolve (Seeley, *C. N.* 23, 169; concerning solubilities of other elements and salts *v.* Gore *l.c.*).—II. Ammonia gas. 1. *Heat* decomposes NH_3 partially into N and H; when the gas is passed through an iron or porcelain tube, decomposition begins at about 500°; the nature of the hot surface exerts a most marked influence on the extent of decomposition; the decomposition is, however, never quite complete (Ramsay a. Young, *C. J.* 45, 88). A spiral of Pt heated by an electric current also decomposes NH_3 (Grove, *A.* 63, 1).—2. The *electric discharge* decomposes NH_3 slowly, but *induction sparks* from a large Ruhmkorff's coil more quickly; the decomposition is not quite complete (Deville, *A.* 135, 104; Buff a. Hofmann, *ibid.* 113, 132).—3. NH_3 is decomposed, into N and H, by passage over several *metals* at 700° or so, *e.g.* Au, Pt, Ag, Fe, Cu, &c.; some metals, *e.g.* Ti, combine with the N; the alkali metals set free $\frac{1}{3}$ of the H producing compounds of the form NH_2M: the compound NH_2K is decomposed at a red heat giving NK_3 and NH_3; water acts on it to produce KOH and NH_3 (*v.* Potassium).—4. Mixed with *oxygen and* submitted to the *electric discharge*, NH_4NO_2 and NH_4NO_3 are formed (Carius, *A.* 174, 31).—5. Mixed with *oxygen and heated*, NH_3 burns to H_2O, H, and N, if the NH_3 is in excess; and to H_2O, N, and NH_4NO_3, if the O is in excess (*v.* Hofmann, *A.* 115, 283; Heintz, *ibid.* 130, 102). The flame examined spectroscopically shows characteristic lines, especially one near D (Dibbits, *P.* 122, 521). 6. *Ozone* oxidises NH_3 chiefly to NH_4NO_3 and NH_4NO_2 (Carius, *A.* 174, 31).—7. A *platinum wire* heated in NH_3 mixed with air produces NH_4NO_2, if oxygen is passed into the NH_3 red fumes of N oxides are also produced.—8. Ammonia reacts with N_2O_3 and Cl_2O_3 to form H_2O, N, NH_4NO_2 or NH_4NO_3, and Cl.—9. *Metallic oxides* reducible by H are usually also reduced by NH_3 with formation of metal, N, and H_2O, sometimes with formation of metallic nitrides.—10. NH_3 reacts with many *metallic oxides and haloid salts* to form compounds, either of NH_3 with the metallic salt — *e.g.* $PtCl_2.4NH_3$, $CuSO_4.2NH_3$—or compounds in which part of the H of NH_3 is replaced, *e.g.* NH_2HgCl (*v.* Ammonium Compounds; also the several metals). 11. *Chlorine, bromine,* and *iodine* react energetically with NH_3 to produce NH_4X (X = Cl, Br, or I), and N. NH_3 combines with cooled I to form a brown liquid which is decomposed by water with production of NH_4IAq and explosive iodide of nitrogen [? NI_3] (*v.* Nitrogen).—12. *Sulphur* absorbs NH_3; on heating N is set free and ammonium sulphide formed (Brunner, *D.P.J.* 150, 371).—13. *Carbon* heated in a stream of NH_3 forms NH_4CN and H, sometimes also CH_4.—14. *Boron* heated in a stream of NH_3 form BN (*v.* Boron), and H.—15. NH_3 combines with *acids* (H_2SO_4, HCl, &c. &c.) to form ammonium salts ($(NH_4)_2SO_4$, NH_4Cl, &c. &c., *q.v.*; *v.* also *Combinations*, No. 4).—16. With many *organic anhydrides* NH_3 combines to form the ammonium salts of amic acids, *q.v.* NH_3 also acts on several *inorganic anhydrides* and *acid chlorides* to form bodies more or less analogous to the amic acids; thus with $SO_2OH.Cl$ ammonia forms $NH(SO_2.ONH_4)_2$—the NH_4 salt of imido-sulphuric acid $NH(SO_2OH)_2$—from the salts of this acid are obtained salts of amido-sulphuric, or sulphamic, acid—$NH_2(SO_2OH)$. Again by the action of NH_3 on the acid chloride SO_2Cl_2 it is probable that the amide of sulphuric acid—$(NH_2)_2SO_2$—is produced. So also NH_3 reacts with CO_2 to produce $NH_2(CO.ONH_4)$—the ammonium salt of amidocarbonic, or carbamic, acid. These compounds will be described under the various acids (*v.* Carbamic acid; Sulphamic acid; Sulphur oxyacids, nitrogen derivatives of; &c.).

III. Ammonia solution. 1. *Heat* decomposes NH_3Aq, the whole of the NH_3 being removed as gas.—2. *Chlorine, bromine,* and *iodine* react as with NH_3 gas; chlorine produces a little NH_4ClO_3 (Fresenius, *Fr.* 2, 59).—3. Reacts with *acids* to form ammonium salts (*v. Combinations*, No. 4, also Ammonium compounds).—4. With many *metallic salt solutions* it reacts (similarly to KOHAq) to form an ammonium salt and an oxide or hydroxide of the metal.—5. Heated with *sulphur* in a closed tube ammonium polysulphides are slowly formed (Flückiger, *J. Ph.* [3] 45, 453).—6. Heated with *selenion* in a closed tube, ammonium selenide and selenite are formed; with *tellurium* ammonium tellurite is produced (Flückiger, *l.c.*).

Combinations.—1. Ammonia gas dissolves very freely in *water*, the action is attended with production of heat; $[NH^3,Aq] = 8,130$ (*Th.* 2, 68); a concentrated solution of NH_3Aq diluted with n H_2O develops $\frac{1270}{n}$ units of heat (Berthelot, *A. Ch.* [5] 1, 209). Thomsen (*Th.* 3, 86) gives the following data

NH^3nH^2O,mH^2O

$n+m$	15	25	50
$n = 3{\cdot}2$	319	350	372
„ 15	—	31	53
„ 25	—	—	22

The mass of NH_3 absorbed by water at 0° is not directly proportional to the pressure; for pressures varying from 50 to about 1,000 mm. the mass of NH_3 is less, and for higher pressures it is greater, than that calculated by Dalton and Henry's law (for data *v.* Roscoe a. Dittmar, *A.* 112, 349). As temperature increases the mass of NH_3 becomes more nearly directly proportional to the pressure, until at 100° the proportion is established (for data *v.* Sims, *A.* 118, 345). The S.G. of an aqueous solution of NH_3 varies from ·8844 at 14°, corresponding to 36 p.c. NH_3, to ·9991 (at 14°) corresponding to ·2 p.c. NH_3 (Carius, *A.* 99, 164). Carius gives the annexed table. Determinations made at 14° C.

A solution containing 32 p.c. NH_3 corresponds with the quantity calculated on the assumption that the liquid consists of the compound $NH_4OH.H_2O$ (*v.* Ammonium Compounds).—2. Dry *ammonium nitrate* absorbs NH_3 at all temperatures from −13° to +25° with liquefaction of the salt; heated over 25°, NH_3 is evolved and the substance becomes solid; the liquid at −10° and 760 mm. contains 42·5 grams NH_3 and 100 grams NH_4NO_3, these numbers agree with those calculated from the formula $NH_4NO_3.2NH_3$; the solid at 28°·5 contains NH_4NO_3 and NH_3 in the proportion $NH_4NO_3:NH_3$ (Divers, *Pr.* 21, 109;

Specific gravity	P. C. NH_3	Specific gravity	P. C. NH_3	Specific gravity	P. C. NH_3
0·8844	36·0	0·9133	24·0	0·9520	12·0
0·8848	35·8	0·9139	23·8	0·9527	11·8
0·8852	35·6	0·9145	23·6	0·9534	11·6
0·8856	35·4	0·9150	23·4	0·9542	11·4
0·8860	35·2	0·9156	23·2	0·9549	11·2
0·8864	35·0	0·9162	23·0	0·9556	11·0
0·8868	34·8	0·9168	22·8	0·9563	10·8
0·8872	34·6	0·9174	22·6	0·9571	10·6
0·8877	34·4	0·9180	22·4	0·9578	10·4
0·8881	34·2	0·9185	22·2	0·9586	10·2
0·8885	34·0	0·9191	22·0	0·9593	10·0
0·8889	33·8	0·9197	21·8	0·9601	9·8
0·8894	33·6	0·9203	21·6	0·9608	9·6
0·8898	33·4	0·9209	21·4	0·9616	9·4
0·8903	33·2	0·9215	21·2	0·9623	9·2
0·8907	33·0	0·9221	21·0	0·9631	9·0
0·8911	32·8	0·9227	20·8	0·9639	8·8
0·8916	32·6	0·9233	20·6	0·9647	8·6
0·8920	32·4	0·9239	20·4	0·9654	8·4
0·8925	32·2	0·9245	20·2	0·9662	8·2
0·8929	32·0	0·9251	20·0	0·9670	8·0
0·8934	31·8	0·9257	19·8	0·9677	7·8
0·8938	31·6	0·9264	19·6	0·9685	7·6
0·8943	31·4	0·9271	19·4	0·9693	7·4
0·8948	31·2	0·9277	19·2	0·9701	7·2
0·8953	31·0	0·9283	19·0	0·9709	7·0
0·8957	30·8	0·9289	18·8	0·9717	6·8
0·8962	30·6	0·9296	18·6	0·9725	6·6
0·8967	30·4	0·9302	18·4	0·9733	6·4
0·8971	30·2	0·9308	18·2	0·9741	6·2
0·8976	30·0	0·9314	18·0	0·9749	6·0
0·8981	29·8	0·9321	17·8	0·9757	5·8
0·8986	29·6	0·9327	17·6	0·9765	5·6
0·8991	29·4	0·9333	17·4	0·9773	5·4
0·8996	29·2	0·9340	17·2	0·9781	5·2
0·9001	29·0	0·9347	17·0	0·9790	5·0
0·9006	28·8	0·9353	16·8	0·9799	4·8
0·9011	28·6	0·9360	16·6	0·9807	4·6
0·9016	28·4	0·9366	16·4	0·9815	4·4
0·9021	28·2	0·9373	16·2	0·9823	4·2
0·9026	28·0	0·9380	16·0	0·9831	4·0
0·9031	27·8	0·9386	15·8	0·9839	3·8
0·9036	27·6	0·9393	15·6	0·9847	3·6
0·9041	27·4	0·9400	15·4	0·9855	3·4
0·9047	27·2	0·9407	15·2	0·9863	3·2
0·9052	27·0	0·9414	15·0	0·9873	3·0
0·9057	26·8	0·9420	14·8	0·9882	2·8
0·9063	26·6	0·9427	14·6	0·9890	2·6
0·9068	26·4	0·9434	14·4	0·9899	2·4
0·9073	26·2	0·9441	14·2	0·9907	2·2
0·9078	26·0	0·9449	14·0	0·9915	2·0
0·9083	25·8	0·9456	13·8	0·9924	1·8
0·9089	25·6	0·9463	13·6	0·9932	1·6
0·9094	25·4	0·9470	13·4	0·9941	1·4
0·9100	25·2	0·9477	13·2	0·9950	1·2
0·9106	25·0	0·9484	13·0	0·9959	1·0
0·9111	24·8	0·9491	12·8	0·9967	0·8
0·9116	24·6	0·9498	12·6	0·9975	0·6
0·9122	24·4	0·9505	12·4	0·9983	0·4
0·9127	24·2	0·9512	12·2	0·9991	0·2

Raoult, *C. R.* 76, 1261.—3. Ammonia gas combines with a great many *metallic chlorides, sulphates, &c.*, to form either double compounds or compounds which are best regarded as substituted ammonium salts. (For a slight general sketch *v.* AMMONIUM COMPOUNDS. The several compounds are described in the arts. on the different metals).—4. Ammonia gas or solution combines with *acids* to form well-marked salts isomorphous with the corresponding salts of the alkali metals. The value of the heat of neutralisation of an acid by NH_3Aq is always rather smaller than the value when KOHAq or NaOHAq is used; thus Thomsen (*Th.* 1, 412-421) gives these numbers:

BAq	$[H^2SO^4Aq, BAq]$	$[H^2Cl^2Aq, BAq]$	$[H^2N^2O^6Aq, BAq]$
2KOHAq	31,288	27,504	27,544
2NaOHAq	31,378	27,488	27,364
$2NH_3Aq$	28,152	24,544	27,644

These results are quite in accordance with the view that an aqueous solution of NH_3 contains the compound $(NH_4)OH$, analogous in composition and properties to the hydroxides of the alkali metals (*v.* AMMONIUM COMPOUNDS).

Detection.—Free ammonia is detected: 1. by its smell; 2. by its action on HCl whereby white clouds of NH_4Cl are produced; 3. by its action on paper, *a.* moistened with neutral $HgNO_3Aq$, whereby a black stain (Hg_2O) is formed, *b.* moistened with $CuSO_4Aq$ whereby a sky-blue colour ($CuSO_4.4NH_3$) is produced, *c.* moistened with $MnSO_4Aq$, whereby brown spots (Mn_2O_3) are formed, *d.* steeped in an ethereal solution of alkanna root (Enz, *J.* 1870. 935), whereby a blue colour is produced (Böttger, *J. pr.* 107, 146). The presence of ammonia or ammonium salts can be ascertained by various tests; the following may be mentioned.—4. *Sodium picrate* precipitates yellow ammonium picrate.—5. A solution of *sodium molybdate* containing phosphoric and nitric acids forms a citron yellow pp. (Sonnenschein, *J. pr.* 56, 302).—6. *Nessler's solution*—a strongly alkaline solution of HgI_2 in KIAq—forms a brown pp., or brown colour in *extremely dilute* solution, of $NHg_2I.H_2O$ (Nessler, *C. C.* 1856. 529). All ammonium salts are at least partly volatilised when heated; some give sublimates of the original salt, *e.g.* NH_4Cl; others are decomposed, *e.g.* NH_4NO_3 and NH_4NO_2.

Estimation.—1. Ammonium salts are sometimes estimated in a mixture, all the other constituents of which are non-volatile, by heating a specified quantity and determining the loss of weight.—2. All ammonium salts are decomposed by heating with KOHAq (or NaOHAq) with evolution of NH_3: if organic N-containing compounds which evolve NH_3 by the action of alkalis are absent, it is only necessary to add a weighed quantity of the ammonium compound to an excess of KOHAq, or NaOHAq, which has been boiled and cooled, in a flask connected with a condenser and receiver, and to warm on a sand-bath; NH_3 passes over and is received in dilute HClAq; the NH_4Cl is then transformed into $2NH_4Cl.PtCl_4$ (*v.* No. 3), or the NH_3 is received in a measured quantity—excess—of standardised HClAq, H_2SO_4Aq, or $H_2C_2O_4Aq$, and the residual acid is determined by titration with standard alkali. [A special apparatus is described by Harcourt (*Fr.* 2, 14).] If N-containing organic compounds are present which evolve NH_3 by the action of alkalis, Schlossing

(*A. Ch.* [3] 31, 153) recommends to place the substance with excess of milk of lime over a measured quantity of standard H_2SO_4Aq, under a bell jar, for 48 hours, and then to determine the residual acid by standard alkali.—3. Ammonium salts the acids of which are soluble in alcohol may be estimated by conversion into $2NH_4Cl.PtCl_4$; an excess of nearly neutral $PtCl_4Aq$, free from HNO_3, is added to the solution, the liquid is evaporated at 100°, the residue is washed with alcohol, dried at 100°, and weighed, or it is strongly heated and the residual platinum is weighed. This method is applicable in the presence of salts which form double compounds with Pt soluble in alcohol; it is best that such salts should be chlorides, to insure this the mixture is evaporated with excess of conc. HClAq (it is best to remove sulphuric acid by $Ba(OH)_2$, excess of $Ba(OH)_2$ being afterwards removed by CO_2). In the case of KCl, which forms a salt $2KCl.PtCl_4$ insoluble in alcohol, the mixed Pt salts are weighed, then strongly heated and again weighed, the KCl is dissolved out in water, and the residual Pt is weighed.—4. Ammonium salts are decomposed by alkaline hypochlorites or hypobromites giving off all their N, which may be collected and measured.

$$(2NH_4ClAq + 3NaClOAq = N_2 + 3NaClAq + 3H_2O + 2HClAq).$$

Wöhler employed calcium hypochlorite for the purpose; Knop (*Fr.* 9, 225) used barium or sodium hypobromite (prepared by the action of Br on $Ba(OH)_2Aq$ or on NaOHAq); Schiff has described a special apparatus (*Fr.* 7, 430); Kroeker a. Dietrich (*Fr.* 3, 64; 5, 40) decompose by excess of brominated NaOClAq, and determine the residual hypochlorite by titrating with an alkaline solution of arsenious oxide. (Comp. also Foster, *C. J.* 33, 470.)—5. Minute quantities of NH_3 are determined by the colorimetric process of Nesslerising; a measured quantity of Nessler's reagent —HgI_2 in KIAq made strongly alkaline by KOHAq—is added, and the colour is compared with that produced by an equal quantity of Nessler's solution in an equal volume of water containing a known quantity of ammonia.

M. M. P. M.

AMMONIA, ACTION ON ORGANIC BODIES. 1. Ammonia converts alkyl salts of inorganic acids into amines (*q. v.*).—2. It converts alkyl salts of carboxylic acids into amides (*q. v.*).—3. It converts the oxides of acid radicles into amide and ammonium salt: $Ac_2O + 2NH_3 = AcNH_2 + AcONH_4$.—4. It converts chlorides of acid radicles into amides of the corresponding acids: $AcCl + 2NH_3 = AcNH_2 + NH_4Cl$.—5. It unites with cyanic ethers forming ureas.—6. It unites with thio-carbimides forming thio-ureas.—7. It unites with aldehydes, but in the case of the higher fatty aldehydes and the aromatic aldehydes water is simultaneously split off.—8. It unites with ketones and quinones.—9. Alcoholic NH_3 sometimes removes HCl; thus, it converts isobutylidene chloride $Me_2CH.CHCl_2$, chloro-iso-butylene $Me_2C:CHCl$, and di-chloro-propane $CH_3.CCl_2.CH_3$, into chloro-propylene $CH_3CCl:CH_2$ (Oeconomides, *C. R.* 92, 1235).—10. For its action on oxy compounds see AMINES, *Formation* 10.—11. Ammonia can displace O by NH.

AMMONIAC GUM *v.* GUM.

AMMONIUM COMPOUNDS. Compounds produced by the action of ammonia on acids. The conditions of occurrence in nature, and also of the artificial syntheses, of these salts are referred to in the article AMMONIA, *q. v.* In that article some data are given regarding the absorption of ammonia by water (*Combinations*, No. 1), and regarding the thermal values of the neutralisation of acids by NH_3Aq (*Combinations*, No. 4). The products of the mutual actions of NH_3Aq, and HClAq, H_2SO_4Aq, and other acids—the ammonium salts—are for the most part white crystalline bodies, easily soluble in water, and many of them soluble also in alcohol; they exhibit marked analogies with the salts of potassium. Corresponding ammonium and potassium salts are isomorphous, hence they probably have similar compositions. The ammonium salts are distinguished by their comparatively great volatility; heated, as solids, they are completely volatilised, if the acid of the salt is volatile; if the acid is non-volatile (*e.g.* borate or phosphate), ammonia is evolved. They do not exist as gases; when volatilised they are either decomposed *e.g.* NH_4NO_3, or dissociated *e.g.* NH_4Cl, *q. v.* (*v.* also DISSOCIATION). When gaseous NH_3 acts on gaseous HCl, HBr, or HI, combination occurs with production of much heat and formation of solid compounds NH_3HX, thus (*Th.* 2, 75):

X	(NH^3, HX)
Cl	41,900
Br	45,020
I	43,460

If the solid products of these actions, NH_3HX, are heated to about 450°, a vapour is obtained containing NH_3 and HX; on cooling this vapour the compound NH_3HX is re-formed. Gaseous NH_3 does not combine with HCl, HBr, or HI, at temperatures above about 450°. These facts establish a difference between the ammonium and potassium compounds. This difference is further exhibited in the reactions of the two classes of compounds; the ammonium salts are easily decomposed, *e.g.* by alkalis and alkaline earths, with production of NH_3. On the other hand the properties of NH_3Aq (*v.* AMMONIA, *Properties of*) are so similar to those of KOHAq, and the reactions of acids with these solutions, whether considered thermally or chemically, are so analogous, that there can be little doubt that the composition of ammonium salts is similar to that of potassium salts. This similarity is at once rendered apparent by formulating the former class of salts as compounds of the hypothetical group of atoms NH_4, *ammonium*. Thus we have:

$NH_4.Cl$ isomorphous with and chemically analogous to K.Cl,

$NH_4.NO_3$ isomorphous with and chemically analogous to $K.NO_3$,

$(NH_4)_2.SO_4$ isomorphous with and chemically analogous to $K_2.SO_4$,

$(NH_4)_2.C_2O_4$ isomorphous with and chemically analogous to $K_2.C_2O_4$,

$NH_4.C_2H_3O_2$ isomorphous with and chemically analogous to $K.C_2H_3O_2$.

If this analogy of properties is in all cases supposed to accompany analogy of composition; then NH_3Aq must be formulated as $NH_4.OHAq$. The compound NH_4OH has not been separated

from the solution of NH_3 in water; but this does not prove the non-existence of the compound in this solution. A chemical compound may, and sometimes almost certainly does, exist as a member of a system, and yet it may be incapable of existence apart from the other members of the system. The existence of every compound is conditioned by other factors than the elements which compose it; among these factors, temperature, and the presence or absence of other compounds, are very important. Compounds closely resembling NH_4OH, and undoubtedly derived from NH_4OH, are known as definite solid bodies; they are obtained by replacing the four hydrogen atoms in the complex NH_4OH by alcoholic radicles C_nH_{2n+1} or C_nH_{2n-7}; thus $N(CH_3)_4.OH$, $N(C_2H_5)_4.OH$, and $N[(C_2H_5)_2(C_6H_5)_2]OH$, have been prepared. These bodies closely resemble NaOH and KOH in their properties; their existence and properties are strong arguments in favour of the existence of the compound NH_4OH in aqueous solutions of NH_3. The formulæ $NH_4.OH$, $NH_4.Cl$, $(NH_4)_2SO_4$ &c., then better summarise the properties and reactions, and suggest the analogies, of the ammonium compounds, than the alternative formulæ $NH_3.H_2O$, $NH_3.HCl$, $(NH_3)_2.H_2SO_4$ &c. The name *ammonium* is given to the compound radicle, or group of atoms, NH_4. We do not know that the composition of the molecule of ammonium chloride is represented by the formula NH_4Cl; indeed we do not even know the molecular weight of this, or of any other, ammonium compound. These compounds seem to exist only as solids, or in solution. We are scarcely justified in applying the term molecule to the chemically reacting small particles of solids or liquids, unless the term is used in a wider and vaguer sense than is given to it when we speak of the molecule of a gas (*v.* ATOMIC AND MOLECULAR WEIGHTS). But in saying that the complex or collocation of atoms which forms the reacting weight of ammonium chloride is a combination of an atom of chlorine with the radicle, or group of atoms, ammonium, we mean to imply that, when this complex of atoms reacts with various other kinds of matter, it behaves as if the four atoms of hydrogen were, in some way, more directly and closely related to the atom of nitrogen than to the atom of chlorine. The fact that when the same complex of atoms is heated it separates into two distinct molecules, HCl and NH_3, neither proves nor disproves the correctness of the formula $NH_4.Cl$, and the conception which that formula embodies. Neither does the fact, that no gaseous molecule is known containing a single atom of nitrogen combined with more than three monovalent atoms, disprove the formula $NH_4.Cl$; for the solid compound ammonium chloride presents us with phenomena to which the conceptions regarding the valencies of atoms, which have been gained by the study of gaseous molecules, are not strictly applicable.

In connection with the constitution of ammonium compounds it is of interest to observe that the compound produced by the union of $N(CH_3)_2C_2H_5$ with C_2H_5I appears to be identical with the compound produced by the union of $N(C_2H_5)_2CH_3$ with CH_3I; it seems as if this compound $N[(CH_3)_2(C_2H_5)_2]I$ belonged to the same form or type as $NH_4.I$, $NH_4.Cl$, $NH_4.OH$, &c. (V. Meyer and Lecco, *B.* 8, 233 a. 936).

The group of atoms, NH_4, is evidently chemically comparable with the atoms K, Na, Li, Cs, or Rb; but these are the atoms of strongly positive metals; hence if the group NH_4 could be isolated it might be expected to exhibit properties similar to those of the alkali metals. Experiments have demonstrated the impossibility of the existence of NH_4 uncombined with other atoms; but certain reactions are known which suggest the existence of an alloy of this hypothetical metallic radicle with mercury.

AMMONIUM AMALGAM. If an electric current is passed through conc. NH_3Aq, or NH_4ClAq, the negative electrode consisting of mercury and the positive of a platinum wire, the mercury swells up, sometimes to 20 times its original volume, and becomes pasty so that it may be lifted by the hand, while nitrogen is evolved at the positive electrode. The same result is obtained as regards the mercury, if a piece of solid NH_4Cl is used; also if sodium-amalgam, containing about 1 p.c. Na, is placed in conc. NH_4ClAq—in this case NaClAq is produced. The peculiar, pasty, lustrous, metal-like, substance formed in these experiments is called ammonium-amalgam; at a very low temperature, obtained by solid CO_2 and ether, it is a dark-grey, solid, crystalline, mass; even at $-29°$ it begins to evolve NH_3 and H, and this change proceeds rapidly at moderate temperatures; the two gases always come off in the ratio NH_3 : H.

An amalgam of K with Hg is produced by electrolysis under conditions very similar to those which attend the production of ammonium-amalgam; the analogy between ammonium and potassium is thus carried out here also. Ammonium-amalgam, it is said, does not reduce salts of Ag, Cu, or Fe, as K amalgam does (Landolt, *A. Suppl.* 6, 346). When the amalgam is subjected to increased pressure its volume is found to change almost inversely as the pressure; in this respect then it behaves like a gas rather than a semi-solid compound. The following data are given by Routledge (*C. N.* 26, 210):—

c.c. of Hg in amalgam.	c.c. of amalgam, pressure 762 mm.	Increased pressure applied, in mm. of Hg.	c.c. of amalgam under increased pressure.	c.c. of amalgam calculated by Boyle's law.
14·5	21·0	1524	18·0	17·9
24·4	36·2	1524	31·6	30·9
10·4	18·0	1863	14·7	13·7
23·8	42·2	1026	38·8	38·5
23·8	42·0	2015	32·2	31·6
23·8	36·2	1495	32·6	30·6
29·2	39·5	1989	34·4	35·4

As the pressure increases, the surface of the amalgam becomes brighter, until under large pressures it has the appearance and liquidity of mercury (Seeley, *C. N.* 21, 265). These results point to the existence of gaseous NH_3 or H, or, it may be, gaseous NH_4, in the Hg; but they do not disprove the existence of the atomic group NH_4 in some kind of loose combination with Hg. An alloy of Fe and NH_4

is said by Meidinger (*C. C.* 1862. 78) to be formed when $FeSO_4Aq$ or $FeCl_2Aq$, to which a considerable quantity of NH_4ClAq has been added, is electrolysed by a strong current, the negative electrode consisting of a copper wire.

By electrolysing aqueous solutions of ammonium salts using carbon electrodes, Bartoli a. Papasogli (*G.* 13, 281) obtained benzenecarboxylic acids and a compound of C, H, O, and N, resembling mellogen.

Of the ammonium compounds we have here to consider the *bromide, chloride, fluorides, iodides, selenides, telluride,* and *sulphides*; the others will be considered under the headings CARBONATES, NITRATES, SULPHATES, &c. The hydroxide, known only in aqueous solution, has been already treated of in the art. AMMONIA.

Ammonium bromide. NH_4Br. Mol. w. unknown; does not exist as a gas, but is dissociated by heat into $HBr+NH_3$. S.G. $\frac{0}{4}$° 2·379 (Schröder, *P.* 106, 242). S. G. $\frac{15}{4}$° 2·327 (Eder, *Sitz. W.* 82 (2), 1284). V. D. at 440° to 860° 24·4 (Deville and Troost, *C. R.* 49, 239; 56, 881). S. (10°) 66·2; (16°) 72; (30°) 81·1; (50°) 94·1; (100°) 128·2. S. (alcohol, S.G. ·806, 15°) 3·1; (75°) 10·5. S. (ether S. G. ·729)·12 (Eder, *l.c.*). $[NH^3, HBr] = 45,020$; $[N, H^4, Br] = 65,318$ (*Th.* 2, 75). $[NH^4Br,Aq] = -4380$ (*Th.* 3, 197). S.V.S. 41·7.

Formation.—1. By adding HBr or HBrAq to NH_3 or NH_3Aq. 2. By the action of Br on NH_3Aq; $4NH_3Aq + 3Br = 3NH_4BrAq + N$: on evaporation, crystals are obtained.

Properties and Reactions.—White crystals; soluble in water; the act of solution is attended with absorption of much heat. Exposed to moist air turns yellow, and acquires an acid reaction. An aqueous solution gives off ammonia at moderately low temperatures.

Troost (*C. R.* 92, 715) describes three compounds, $NH_4Br.xNH_3$, $x=1$, 3, and 6, obtained by the action of excess of NH_3 on warm NH_4Br; the dissociation-phenomena of these compounds have been studied by Roozeboom (*R.T.C.* 4, 361).

Ammonium chloride. NH_4Cl. (*Sal ammoniac.*) Mol. w. unknown; does not exist as gas, but is dissociated by heat into NH_3+HCl. S.G. 1·52 (Schröder, *P.* 106, 242). V.D. at 350° = 14·4, at 1040° = 14·5 (Deville a. Troost, *C. R.* 49, 239; 56, 891); but vapour consists of equal volumes of NH_3 and HCl (*v. Reactions*, No. 1). S.H. (15° to 45°) ·373 (Kopp, *T.* 155, 71). S.H. (23° to 100°) ·3908 (Neumann, *P.* 126, 123). C.E. (cubical, 0° to 40°) ·00018764 (Fizeau, *C. R.* 64, 314). S.V.S. 35·2. S. (0°) 28·4; (10°) 32·8; (110°) 77·2; S. increases approximately 4·4 parts for each 10° (Alluard, *C. R.* 59, 500). S. (alcohol S.G. ·939, 8°) 12·6; (56°) 30·1 (Gerardin, *A. Ch.* [4] 5, 129). $[NH^3, HCl] = 41,900$; $[NH^3Aq, HClAq] = 12,270$; $[N, H^4, Cl] = 75,790$ (*Th.* 2, 75). $[NH^4Cl,Aq] = -3,880$ (*Th.* 3, 197).

$[NH^4Cl. n H^2O, m H^2O]$ (*Th.* 3, 109).

$n+m$ =	25	50	100	200
n = 10	−87	−121	−129	−129
„ 25	—	− 34	− 42	− 42
„ 50	—		− 8	− 8
„ 100	—		—	0

Occurrence.—In small quantities, in the neighbourhood of volcanoes, and in fumaroles; in some animal secretions, *e.g.* saliva.

Formation.—1. By mixing HCl and NH_3 in equal volumes. 2. By the action of HCl on N and H, under the influence of the electric discharge, or when heated and quickly cooled (for details *v.* AMMONIA, *Formation*, Nos. 1, 2, and 3).—3. By the decay, or destructive distillation, of various N-containing organic matters.

The name *Sal ammoniacum* seems to have been given by the earlier chemists to rock-salt; Geber, probably latter part of 8th century, prepared ammonium chloride from urine and common salt; towards the end of the seventeenth century the name *Sal ammoniacum* came to be applied to ammonium chloride. The salt was prepared in Egypt by sublimation from the sooty deposit obtained by burning camel's dung. The first manufactory of sal ammoniac in this country was established at Edinburgh in 1756.

Preparation.—Crude ammonium carbonate obtained by the dry distillation of bones, horn, blood, &c., or gas coal, is decomposed by hot milk of lime, and the NH_3 produced is led into HClAq, the liquid is boiled down, and the crude NH_4Cl is purified by solution, filtration through animal charcoal, re-crystallisation, and sublimation. For details of preparation of pure NH_4Cl *v.* AMMONIA, *Preparation No.* 3.

Properties.—Pure ammonium chloride is a white, inodorous, salt, with a pungent taste; it crystallises from aqueous solutions in small cubes or octahedra which gather together into feathery masses (*v.* further, Naumann, *J. pr.* 50, 11 and 310). By sublimation and rapid cooling it is obtained as a loosely cohering powder consisting of minute octahedra; the ordinary sublimed salt has been partially fused and appears as a semi-translucent mass of fibrous crystals. It is very tough, and cannot be powdered; sal ammoniac is best obtained in fine powder by evaporating a solution to dryness with constant stirring. It is easily soluble in water (*v.* data at beginning of article); a conc. aqueous solution boils at 115·8° at 768 mm. (Alluard, *C. R.* 59, 500); S.G. $\frac{15}{4}$° of conc. NH_4ClAq containing 26 p.c. NH_4Cl is 1·0752 (Michel a. Krafft, *A. Ch.* [3] 41, 471). Tables of S.G. of NH_4ClAq are given by Gerlach (*J.* 1859. 42), and Schiff (*A.* 110, 74). On heating NH_4ClAq of 10·6 p.c. to 37° NH_3 is given off in the water-vapour (Leeds, *Am. S.* [3] 7, 197); as temperature increases the decomposition of NH_4Cl probably increases also (*v.* Fittig, *A.* 128, 189; Dibbits, *B.* 5, 820; Brücke, *J. pr.* 104, 481).

Reactions.—1. When NH_4Cl is *heated* it vaporises, but the vapour is found to consist of HCl and NH_3 (*v.* Pebal, *A.* 123, 199; Than, *A.* 131, 129; Wanklyn, *P.M.* [4], 29, 112; Wurtz, *J.* 1859. 30; Deville a. Troost, *C. R.* 49, 239; 56, 891; Tommasi, *B.* 14, 353). The density of the vapour is 12·9 according to Bineau (*A. Ch.* [2] 68, 416); 14·4 at 350°, and the same at 1040°, according to Deville and Troost (*C. R.* 49, 239; 56, 891). Than (*l.c.*) has shown that HCl does not combine with NH_3 at 350° or higher temperatures.—2. NH_4ClAq is decomposed by *chlorine* with formation of HCl and nitrogen chloride (*q. v.*).—3. Heated with *iron, zinc,* or better with *potassium*, NH_4Cl is decomposed with production of metallic chloride, NH_3, and H; in presence of air and moisture the reaction proceeds rapidly with formation of metallic chloride

or oxychloride and NH_3.—4. Many *metallic oxides* decompose NH_4Cl with formation of chlorides, and NH_3; in some cases—*e.g.* oxides of Hg, Pt, Au &c.—the chloride combines with a portion of the NH_4Cl to form a double compound. 5. *Alkaline carbonates* decompose NH_4Cl when heated with volatilisation of ammonium carbonate. *Calcium carbonate*, especially when freshly precipitated, dissolves readily in NH_4ClAq; on heating, ammonium carbonate is evolved.—6. *Crystallised sodium sulphate* partially decomposes NH_4Cl when the two are mixed together by rubbing, NaCl and $(NH_4)_2SO_4$ being formed and partly dissolving in the water which comes from the sodium sulphate crystals.—7. *Sulphuric anhydride* vapour is absorbed by powdered NH_4Cl, on warming HCl is evolved and $SO_2NH_2ONH_4$ is formed; if water is added $(NH_4)_2SO_4$ is produced.—8. The reaction between *acids* and NH_4Cl follows the ordinary course of the interaction of acids with salts of other acids.

Combinations. — 1. NH_4Cl combines with many *metallic chlorides* to form double compounds; *e.g.* $PtCl_4.2NH_4Cl$; $HgCl_2.2NH_4Cl$; $CuCl_2.2NH_4Cl$ &c. (*v.* the several METALS).—2. With an aqueous solution of ICl_3, the compound $NH_4Cl.ICl_3$ is produced (*v.* AMMONIUM IODIDE; *Reactions*, No. 2).—3. According to Troost (*C. R.* 88, 578) when NH_4Cl is heated with a large excess of pure dry *ammonia*, at least two compounds are formed: $HCl.4NH_3$, melting at 7°; and $HCl.7NH_3$, formed at −31° and 750 mm., melting at −18°.

Ammonium fluorides (Marignac, *Ann. M.* [5] 15, 221).

I. NEUTRAL SALT. NH_4F. Mol. w. unknown. $[NH^3Aq, HFAq] = 15{,}200$ $[NH^3, HF] = 30{,}100$ (Guntz, *C. R.* 97, 1483). *Formation.*—1. By mixing HF and NH_3.—2. By heating KF or NaF with NH_4Cl. *Preparation.*—1. By gently heating a *dry* finely powdered mixture of 1 part NH_4Cl with $3\frac{1}{4}$ parts KF in a platinum crucible covered with a lid, which is kept cold by dropping water on to it; the NH_4F sublimes on to the lid.—2. Ordinary HFAq is saturated with NH_3Aq, a little $(NH_4)_2CO_3Aq$ is added, the clear liquid is decanted and evaporated in a platinum dish with repeated additions of small pieces of solid ammonium carbonate. *Properties.*—Hexagonal prisms with strong saline taste; unchanged in dry air, but deliquescent in moist air; easily soluble in water, less soluble in alcohol; an aqueous solution gives off NH_3 and acquires an acid reaction; the dry salt absorbs NH_3 but gives it off again on heating; sublimes readily with previous fusion; etches glass, and must be kept in platinum, silver, or gutta percha, vessels. *Reactions.*—1. When moist, or in solution in water, NH_4F decomposes *silicates* with formation of SiF_4; the same decomposition is effected by the dry salt by heating it with silicates.—2. An aqueous solution is decomposed by *heat*, with formation of the acid salt $NH_4F.HF$ and evolution of NH_3 (*v. infra*).

II. ACID SALT. $NH_4F.HF$. Mol. w. unknown. S.G. 1·21. *Formation.*—1. By evaporating an aqueous solution of NH_4F at 36° to 40° in a platinum dish.—2. By adding excess of NH_3Aq to a solution of fluosilicic acid, and evaporating; as thus obtained the salt is mixed with silica. *Properties.*—Colourless prisms; easily soluble in water; slightly deliquescent; easily volatilised, vapour being very acrid.

Ammonium iodides.

I. NH_4I. Mol. w. unknown; does not exist as gas, but is dissociated by heat into $NH_3 + HI$. S.G.$^{11°}$ 2·498. S.V.S. 58. V.D. (440° to 860°) 38·8, but vapour consists of equal volumes of HI and NH_3. $[NH^3, HI] = 43{,}462$; $[N, H^4, I] = 49{,}313$ (*Th.* 2, 75). $[NH^4I, Aq] = -3{,}550$ (*Th.* 3, 197). *Formation.*—1. By mixing equal volumes of HI and NH_3, or by acting on HIAq with NH_3Aq.—2. By decomposing Fe_2I_6Aq by $(NH_4)_2CO_3Aq$, or BaI_2Aq by $(NH_4)_2SO_4Aq$. *Preparation.*—1. Hot saturated solutions of $(NH_4)_2SO_4$ and KI, equal equivalents, are mixed; after cooling, alcohol equal to 15 p.c. of the water used is added; the liquid is filtered after 12 hours, and evaporated with addition of a little NH_3Aq from time to time (Jacobsen, *C. C.* 1864. 192).—2. A solution of $27\frac{1}{2}$ parts KI in 48 parts H_2O is mixed with a solution of 22 parts tartaric acid in 48 parts water, the mixture is placed in a freezing mixture to separate $KHC_4H_4O_6$, the filtrate is evaporated at 100° with addition of a little $(NH_4)_2CO_3$ (Beyer, *D. P. J.* 171, 467). *Properties.*—Colourless cakes, very soluble in water and alcohol; deliquesces in moist air, and becomes yellow through separation of I, and loss of NH_3; may be sublimed unchanged in absence of air. *Reactions.*—1. NH_4IAq is easily decomposed by dilute *acids*; the solid compound is decomposed by dry HCl gas at high temperatures, at 360° about $\frac{1}{20}$th, at 440° about $\frac{1}{6}$th, at a dark red heat about $\frac{1}{3}$ths, of the NH_4I being decomposed (Hautefeuille, *C. R.* 64, 704).—2. *Chlorine* led into saturated NH_4IAq produces long, golden-yellow, needles of $NH_4Cl.ICl_3$ (Filhol, *J. Ph.* 25, 441); this compound is decomposed by gentle heating into ICl_3 and NH_4Cl.—3. By heating in *ammonia*, the compounds $NH_4I.xNH_3$ $x = 1$, 3, and 6, are obtained according to Troost (*C. R.* 92, 715).

II. According to Guthrie (*C. J.* [2] 1, 239) a compound of NH_4I with I—$NH_4I.I$—is obtained, as a brownish-black liquid, soluble in alcohol, ether, CS_2, and KIAq, less soluble in $CHCl_3$, when I is added in small quantities to a conc. solution of NH_4NO_3 with which $\frac{1}{3}$ equivalent of KOH has been mixed. $NH_4I.I$ easily separates in dry air into NH_3 and I; water or dilute alkali produces iodide of nitrogen, NH_4I, and HI; mercury acts on it to form HgI_2 and NH_3; aqueous solutions of acids produce NH_4 salts and separate I.

Johnson (*C. J.* 33, 397) describes a compound of NH_4I and I the composition of which agrees with the formula NH_4I_3. It is produced by adding I to NH_4I in presence of a little water until no more I dissolves. It forms dark-blue, somewhat deliquescent, prisms; S.G. 3·749; soluble in a little water, decomposed on dilution with precipitation of I. This compound seems to form a double salt with KI, viz. $5NH_4I_3.KI$, obtained by passing NH_3 into the mother liquor from which KI_3 has separated.

Ammonium selenides $(NH_4)_2Se$, and $(NH_4)SeH$ (Bineau, *A. Ch.* [2] 67, 229). Neither has been gasified and therefore *mol. ws.* are unknown. NH_3 has no action on Se, but readily combines with H_2Se; when excess of NH_3 is used 2 vols. combine with 1 vol. H_2Se and produce $(NH_4)_2Se$, when excess of H_2Se is used equal vols. of the

gases combine and form $NH_4.HSe$. These compounds are white solids which soon turn red by exposure to air or when dissolved in air-containing water; both smell of NH_3 and H_2Se and appear easily to undergo change; their aqueous solutions probably contain polyselenides although none of these has been isolated; the products of the distillation of K_2Se with NH_4Cl probably also contain ammonium polyselenides.

Ammonium telluride $NH_4.HTe$. White leaf-shaped crystals; easily soluble in water, volatilised at 80°. Formed by the direct union of NH_3 and H_2Te (Bineau, *A. Ch.* [2] 67, 229).

Ammonium sulphides, and Sulphydrate or Hydrosulphide. Five solid sulphides, and a hydrosulphide, of ammonium are known; their compositions are expressed by the formulæ NH_4HS, $(NH_4)_2S$, $(NH_4)_2S_2$, $(NH_4)_2S_4$, $(NH_4)_2S_5$, $(NH_4)_2S_7$; none of these exists in the gaseous state; the first and second, which have been more studied than the others, are dissociated by heat, into NH_3+H_2S, and $2NH_3+H_2S$, respectively. All the ammonium sulphides are soluble in water, they very easily undergo change at ordinary temperatures, usually giving off NH_3, and H_2S which is often partly decomposed with precipitation of S. They are all decomposed by dilute acids with precipitation of white amorphous S, evolution of H_2S, and formation of an ammonium salt of the reacting acid. These sulphides act as salt-forming or basic compounds towards such acidic sulphides as As_2S_3, As_2S_5, Sb_2S_3 &c. (*v. infra*: also ARSENIC, and ANTIMONY, THIO-ACIDS). According to Berzelius any one of the ammonium sulphides, except $(NH_4)_2S_7$, can be prepared by gently heating the corresponding sulphide of potassium with sal ammoniac; in every case except that of K_2S_5 the NH_4Cl must be in excess, else part of the ammonium sulphide formed is decomposed with production of S (NH_3 and H) which combines with the potassium sulphide to form K_2S_5. Little or nothing is known of the physical constants of these compounds; the following thermal data are given, but, by reason of the instability of the sulphides and the indirect methods by which the numbers have been obtained, they must be accepted with caution:—

H.F. of solids from gaseous N and H, and solid S.

$(NH_4)_2S_2=69,000$ }
$(NH_4)_2S_4=69,600$ } (Sabatier, *C. R.* 91, 53)
$(NH_4)_2S_5=69,400$ (Sabatier, *A. Ch.* [5] 22, 73).

The tetra- and penta-sulphide dissolve in water with absorption of about 8,000 gram-units of heat per formula-weight of the sulphide.

The sulphides of ammonium have been studied chiefly by Fritzsche (*J. pr.* 24, 460; 32, 313).

Preparation.—NH_4HS is prepared by the reaction of equal volumes of NH_3 and H_2S at the ordinary temperature, or at temperatures not lower than −10°. An aqueous solution of NH_4HS is obtained by saturating NH_3Aq with H_2S in absence of air.

$(NH_4)_2S$ is prepared by cooling a mixture of 2 vols. NH_3 and 1 vol. H_2S to −18°; or by distilling K_2S with excess of NH_4Cl and cooling the distillate to −18°.

$(NH_4)_2S_2$ is obtained by passing vapour of S and of NH_4Cl through a hot porcelain tube and then into a well cooled receiver. An aqueous solution may be prepared by dissolving S in $(NH_4)_2S$ Aq in the proportion $(NH_4)_2S$:S.

$(NH_4)_2S_5$: when NH_4HSAq (*v. supra*) is digested with S, the solution saturated with NH_3, and then with H_2S, more S added, and saturation with NH_3 and then with H_2S repeated, the whole liquid sets to a crystalline mass; if this is heated to 40°–50° a clear liquid is produced from which, on gradual cooling, large crystals of $(NH_4)_2S_5$ separate out.

$(NH_4)_2S_4$: if the mother liquor from the crystals of $(NH_4)_2S_5$ is surrounded by a freezing mixture, and treated first with NH_3 and then with H_2S a crystalline magma is formed; on warming a clear liquid is produced from which crystals of $(NH_4)_2S_4$ are deposited.

$(NH_4)_2S_7$ is obtained by the gradual decomposition of $(NH_4)_2S_5$ in dry, slightly warm, air; it is also formed when a solution of $(NH_4)_2S_5$ in its mother liquor (*v. supra*) is placed under a large bell jar for some time.

Properties and Reactions.—NH_4SH: hard, white, plates or needles; very soluble in water, and easily volatilised. V.D. at 56° 12·8, which corresponds with equal vols. of H_2S and NH_3 (Deville a. Troost, *C. R.* 56, 891). Aqueous solution is colourless, but soon changes in air from absorption of O, which decomposes a part of the NH_4HS with formation of H_2O, NH_3, and S; some of the S acts on the remaining NH_4HS to form $(NH_4)_2S_2$, another part of the S is oxidised to $H_2S_2O_3$, and a portion of it is usually deposited. This process proceeds if exposure to air is prolonged; the $(NH_4)_2S_2$ is slowly decomposed, until finally a solution of $(NH_4)_2S_2O_3$ in NH_3Aq, mixed with solid S, is the result. NH_4HSAq reacts with most metallic salts in solution to form sulphides of the metals; it also reacts with acidic metallic sulphides to form ammonium thio-salts, with evolution of H_2S, *e.g.* $As_2S_3 + 2NH_4SHAq = 2NH_4AsS_2Aq + H_2S$ (*v.* ARSENIC, THIO-ACIDS OF).

$(NH_4)_2S$: white, lustrous, crystals; easily soluble in water, forming a colourless liquid which easily decomposes with evolution of NH_3 and formation of NH_4HS. V.D. 18·2 (calculated for 2 vols. NH_3 + 1 vol. H_2S = 17·0) (Deville a. Troost, *C. R.* 56, 891). Reacts as a strongly marked base towards acidic sulphides to form ammonium thio-salts.

$(NH_4)_2S_4$: sulphur-yellow crystals, easily soluble in water and alcohol. Stable only in an atmosphere saturated with NH_3 and H_2S; easily decomposed in air with evolution of NH_3 and H_2S. A saturated aqueous solution is fairly stable; more dilute solutions, and solutions in alcohol, soon precipitate S. When heated, NH_4HS and S are formed.

$(NH_4)_2S_5$: orange-red prismatic crystals, easily soluble in water and alcohol. These solutions are very unstable, decomposing into $(NH_4)_2S_2$, S, H_2S, and NH_3, and after some time also $(NH_4)_2S_2O_3$. In dry air the crystals give off NH_3 and NH_4HS and are changed into $(NH_4)_2S_7$.

$(NH_4)_2S_7$: ruby-red crystals, much more stable than any of the lower sulphides; decomposed at about 300°; soluble in water forming a fairly stable liquid which is only slowly decomposed by HClAq.

The liquid known as *fuming liquor of Boyle*,

or volatile liver of sulphur, chiefly consists of a mixture of various ammonium polysulphides; obtained by distilling a mixture of 1 part S, 2 parts NH_4Cl, and 3 parts CaO. It is a dark yellow, strongly smelling, and strongly fuming, liquid. It dissolves sulphur and then no longer fumes in air.

Ammonia reacts with many metallic salts to form compounds, several of which behave as if they were derivatives of ammonium chloride, sulphate, &c., rather than double compounds of ammonia with the metallic salts in question. Thus NH_3 and $PtCl_2$ form the crystalline compound $PtCl_2.4NH_3$; by the action of H_2SO_4 on this, HCl is evolved, and there is produced $PtSO_4.4NH_3$; decomposed by $Ba(OH)_2Aq$ this compound yields $Pt(OH)_2.4NH_3$, which loses H_2O when heated, with production of $PtO.4NH_3$. The compound $Pt(OH)_2.4NH_3$ is a markedly alkaline body, resembling NaOH or KOH; it neutralises 2 equivalents of a monobasic acid. The compounds $PtCl_2.4NH_3$, $PtSO_4.4NH_3$, and $Pt(OH)_2.4NH_3$, can scarcely be regarded as double compounds of ammonia and platinum salts; their reactions are better suggested by supposing them to be derivatives of ammonium compounds, obtained by replacing part of the hydrogen by platinum. The name platinammonium has been given to the hypothetical radicle

$$N_2H_6Pt. \quad \left(Pt{<}\begin{matrix}NH_3\\NH_3\end{matrix}\right).$$

The chloride of this radicle would be $N_2H_6PtCl_2$; if two hydrogen atoms in the group N_2H_6Pt are supposed to be replaced by two ammonium groups (NH_4) we get the hypothetical radicle ammonium-platinammonium $N_2H_4(NH_4)_2Pt$. The compounds $PtCl_2.4NH_3$, $PtSO_4.4NH_3$, and $Pt(OH)_2.4NH_3$ may be regarded as compounds of this radicle; thus $N_2H_4(NH_4)_2Pt.Cl_2$, $N_2H_4(NH_4)_2Pt.SO_4$, $N_2H_4(NH_4)_2Pt.(OH)_2$.

Compounds are obtained by the action of NH_3Aq on Hg_2Cl_2 and $HgCl_2$, respectively, which have the composition Hg_2NH_2Cl and $HgNH_2Cl$; these react as derivatives of NH_4Cl in which H_2 is replaced by Hg_2 and by Hg, respectively. The name mercuro-ammonium is sometimes given to the hypothetical radicle NH_2Hg_2, and the name mercuri-ammonium to the hypothetical radicle NH_2Hg.

A great many bodies are known the reactions and relations of which can be gathered together into one point of view by considering them as compounds of various hypothetical radicles derived from NH_4, N_2H_8, N_3H_{12}, &c., by replacement of part of the hydrogen by various metals. These compounds will be described under the headings of the various metals (*v.* more particularly the CHROM-AMMONIUM-, COBALT-AMMONIUM-, COPPER-AMMONIUM-, MERCURY-AMMONIUM-, and PLATINUM-AMMONIUM-, COMPOUNDS; in the articles CHROMIUM, COBALT, COPPER, MERCURY, and PLATINUM respectively).

Ammonium salts, *i.e.* derivatives of acids obtained by replacing H by the group NH_4, are described under the various headings CARBONATES, NITRATES, SULPHATES, &c. &c. The principal salts are the following:—*Antimonate; arsenate, arsenite; borate; bromate, &c.; carbamate; carbonates; chlorates, chlorite, &c.; chromates; cyanates; cyanide; iodate, periodate, &c.; molybdates; nitrate, nitrite, &c.; phosphates; selenite, &c.; silicates; sulphamate, &c.; sulphates, sulphites, &c.; tantalate; tellurates; thioarsenates, thiocyanates, thiosulphates, &c.* For an account of the general properties of these salts *v.* beginning of present article.

M. M. P. M.

AMOXY-. Contraction for amyl derivative of OXY-.

AMYDECYLENIC ACID *v.* DECENOIC ACID.

AMYGDALIC ACID $C_{20}H_{26}O_{12}$ or $C_{20}H_{28}O_{13}$. Formed by boiling amygdalin with baryta. Deliquescent crystalline mass, insol. alcohol, and ether. By boiling with H_2SO_4 and MnO_2 it yields formic acid, CO_2, and benzoic aldehyde (Liebig a. Wöhler, *A.* 22, 11; 66, 240; Schiff, *A.* 154, 348).

Acetyl derivatives $C_{20}H_{21}Ac_4O_{13}$ and $C_{20}H_{21}Ac_7O_{13}$ (S.).

AMYGDALIN $C_{20}H_{27}NO_{11}3aq.$ [200°]; after solidifying it melts at 125°–130° (Wöhler, *A.* 41, 155). Mol. w. 511. S. 8·5 at 12°. $[\alpha] = 35{\cdot}5°$.

Occurrence.—In bitter almonds (Robiquet a. Boutron, *A. Ch.* [2] 44, 352); to a small extent in sweet almonds; in laurel leaves (*Cerasus lauro-cerasus*); in the leaves, blossoms, and bark of the birdcherry (*Prunus padus*); in young shoots of the apple tree; and in the kernels of apples, pears, and peaches (Riegel, *A.* 48, 361; Wicke, *A.* 79, 79; 81, 241; Lehmann, *N. R. P.* 23, 449).

Preparation.—The almond-cake from which the fatty oil of almonds has been removed by pressure is extracted with boiling alcohol; the filtrate is concentrated and the amygdalin ppd. by ether.

Properties.—White pearly scales or thin prisms (from water). Insol. ether.

Reactions.—1. Under the influence of emulsin or of boiling dilute H_2SO_4 it is split up into benzoic aldehyde, prussic acid, and glucose (Liebig a. Wöhler, *A.* 22, 17):
$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6$.—2. $KMnO_4$ forms cyanic and benzoic acids.—3. *Potash* or *baryta* form amygdalic acid.—4. Conc. HCl gives mandelic acid, glucose, and NH_3.—5. PCl_5 gives CyCl and benzylidene chloride.—6. Zn and dilute hydrochloric acid give $C_6H_5.CH_2.CH_2.NH_2$ (Fileti, *B.* 12, 297).

Acetyl derivative $C_{20}H_{20}Ac_7NO_{11}$. Long needles (from alcohol); insol. water (Schiff; *A.* 154, 338).

Amorphous amygdalin has been described by Winckler (*B. J.* 20, 428), Neumann (*B. J.* 23, 503), Simon (*A.* 31, 263), and Lehmann (*loc. cit.*).

AMYL C_5H_{11}. *Pentyl.* A monovalent basylous radicle which can occur in eight forms:
n-amyl, $CH_3.CH_2.CH_2.CH_2.CH_2$;
iso-butyl-carbinyl $(CH_3)_2CH.CH_2.CH_2$;
sec-butyl carbinyl, $(CH_3)CH(C_2H_5).CH_2$;
tert-butyl-carbinyl $(CH_3)_3C.CH_2$;
methyl-*n*-propyl-carbinyl, $CH_3.CH_2.CH_2C(CH_3)H$;
methyl-isopropyl-carbinyl, $(CH_3)_2CH.C(CH_3)H$;
di-ethyl-carbinyl $(C_2H_5)_2CH$;
and di-methyl-ethyl-carbinyl $(CH_3)_2(C_2H_5)C$.
Ordinary amyl alcohol is a mixture of *iso*-butyl-carbinol and sec-butyl carbinol, and it is from this mixture that most of the amyl compounds have been prepared. The term 'iso-amyl' compounds will, for the sake of brevity, be used in this dictionary to denote the mixture of amyl

compounds prepared from this source. Inasmuch as the proportion of the two constituents of 'isoamyl' alcohol varies with its source, 'isoamyl' compounds prepared by different chemists can hardly be expected to possess identical physical characters. Amyl derivatives of hydroxylic carbon compounds are described under the compounds of which they are the ethers.

Di-amyl $(C_5H_{11})_2$ or $C_{10}H_{22}$ *v.* DECANE.

AMYL-ACETYLENE *v.* HEPTINENE.

AMYL ALDEHYDE *v.* VALERIC ALDEHYDE.

AMYL ACETATES $C_7H_{14}O_2$. *Pentyl acetates.* Mol. w. 130.

Preparation. — Similar to that of ethyl acetate, p. 14.

***n*-Amyl acetate.** (147·6°) (Gartenmeister, *A.* 233, 260); (148·4°) at 737 mm. (Lieben a. Rossi, *A.* 159, 74). S.G. $\frac{0}{0}$ ·8948; $\frac{20}{20}$ ·8774 (G.). C.E. (0°–10°) ·00106 (G.). S.V. 173·8 (G.). Prepared from *n*-amyl iodide and silver acetate.

Iso-amyl acetate. (137·6°) at 745 mm.; (138·9°) (R. Schiff, *A.* 220, 110). S.G. $\frac{15}{4}$ ·8762 (Mendeléeff, *J.* 1860, 7); $\frac{20}{4}$ ·8561 (Brühl). μ_β 1·4088 (B.). R∞ 59·7 (B.) S.V. 174·6 (S.). Is largely used as a flavouring agent to imitate jargonelle pears.

Methyl-propyl-carbinyl acetate. (133°–135°) (Wurtz, *A.* 148, 132); (134°–137°) (Schorlemmer, *A.* 161, 269). S.G. $\frac{0}{}$ ·922 (W.).

Methyl-isopropyl-carbinyl acetate. (125°) (Wurtz, *A.* 129, 367).

Di-ethyl-carbinyl acetate. (132°) at 741mm. S.G. $\frac{0}{}$ ·909 (Wagner a. Saytzeff, *A.* 175, 306).

Tert-amyl acetate. (124°) at 750 mm. S.G. $\frac{0}{}$ ·891 (Flawitzky, *A.* 179, 348). Decomposed by heat into amylene and acetic acid (Menschutkin, *C. R.* 95, 648).

AMYL ALCOHOLS $C_5H_{12}O$. Mol. w. 88. Theory indicates 8 amyl alcohols (*v.* AMYL), viz.: 4 primary, 3 secondary, and 1 tertiary. One of these, tert-butyl carbinol, is unknown.

***n*-Amyl alcohol** $CH_3.CH_2.CH_2.CH_2.CH_2.OH$. (137°) at 740 mm. (Lieben a. Rossi, *C. R.* 71, 370); (137·9° i. V.) (Zander, *A.* 224, 81). S.G. $\frac{0}{0}$ ·8282 (Z.). C.E. (0°–10°) ·00091 (Z.) S.V. 123·4 (Z.).

Occurrence.—In fusel oil (Wyschnegradsky, *A.* 190, 350).

Formation.—1. From *n*-valeric aldehyde and sodium amalgam (L. a. R.).—2. From *n*-amyl chloride (Schorlemmer, *A.* 161, 268).

Inactive amyl alcohol

$(CH_3)_2CH.CH_2.CH_2OH$. (130·5°–131·2°) (Lachowicz, *A.* 220, 171); (131·5° cor.) (Perkin). S.G. $\frac{15}{15}$ ·8135; $\frac{25}{25}$ ·8078 (P.). M.M. 5·959 at 18·6° (P.). Fusel oil is a mixture of active and inactive amyl alcohol; they can be more or less separated either by passing HCl into the boiling alcohol, when the inactive alcohol is converted into amyl chloride more readily than its isomeride (Le Bel, *C. R.* 77, 1021); or by means of the barium salts of the two amyl-sulphuric acids, $C_5H_{11}SO_4H$, the active salt being the more soluble in water (Pasteur, *C. R.* 41, 296). The simplest way to obtain an inactive amyl alcohol is carefully to fractionate fusel oil (L.). *The same alcohol can be prepared from isobutyl alcohol by converting it first into valeric acid* (Balbiano, *G.* 6, 229).

Iso-amyl alcohol.

mixture of $(CH_3)_2CH.CH_2.CH_2OH$ and $(CH_3)CH(C_2H_5).CH_2OH$. ***Fermentation amyl alcohol. Fusel oil.*** [c. –134°] (Olszewski, *M.* 5, 128). (130·5°–131°) (R. Schiff, *A.* 220, 102). S.G. $\frac{20}{4}$ ·8104 (Brühl, *A.* 203, 23). S.H. ·679 (Diaconoff, *Bl.* [2] 38, 172). *Latent heat of vaporisation* 123·8 (D.). S. 2·5 at 16°. H.F.p. 74,890 (Thomsen). H.F.v. 71,700 (T.). μ_β 1·4124. R∞ 43·08. S.V. 122·7 (S.). *Critical temperature* 307° (Pawlewski, *B.* 16, 2634).

Occurrence.—Formed in small quantity in the alcoholic fermentation of saccharine liquids. Isoamyl angelate and isoamyl tiglate occur in Roman oil of chamomile (Köbig, *A.* 195 99).

Properties.—Poisonous liquid with powerful odour. Its detection in alcohol is described on p. 96. It burns with smoky flame.

Decomposition.—1. Its vapour led through a *red-hot tube* produces acetylene, ethylene, propylene, and butylene (Wurtz, *A.* 104, 242).—2. S_2Cl_2 gives amyl chloride and amyl sulphite (Carius a. Fries, *A.* 109, 1).—3. PCl_3 and PCl_5 form amyl chloride.—4. *Potash-lime* at 220° gives hydrogen and potassic valerate.—5. $ZnCl_2$ produces amylene (*q. v.*). Hot H_2SO_4 and P_2O_5 act similarly.—6. Poured upon *bleaching powder*, it reacts in less than an hour; the distillate decomposes with evolution of Cl_2 and HCl, and then contains amyl alcohol, valeric aldehyde, and amyl valerate (Goldberg, *J. pr.* [2] 24, 116).

Compounds.—$(C_5H_{12}O)_2SnCl_4$. Deliquescent crystalline plates, decomposed by water (Bauer a. Klein, *A.* 147, 249).—$C_5H_{12}O,SbCl_5$.—Crystalline.—$(C_5H_{12}O)_3CaCl_2$ (Heindl, *M.* 2, 209).

Sodic amylate, $C_5H_{11}NaO,2C_5H_{12}O$ (Fröhlich, *A.* 202, 295). At 165° it combines with CO forming sodic isovalerate and the sodium salt of an acid $C_{10}H_{18}O_2$. CO passed over a mixture of $NaOC_5H_{11}$ and NaOAc at 180° produces sodic formate and the sodium salts of a variety of acids, the principal being iso-heptoic acid (*q. v.*) formed by substitution of H of acetic acid by C_5H_{11}. Another product is oxy-vinyl-heptoic or oxy-ennenoic acid (*q. v.*). An acid crystallising in needles $C_{11}H_{18}O_4$ [139°] is also formed; its empirical formula is that of di-acetyl-heptoic acid (Poetsch, *A.* 218, 56).

Potassium amylate $C_5H_{11}OK$. White silky crystals (de Forcrand, *C. R.* 104, 68).

Thallium amylate $C_5H_{11}OTl$. S.G. 2·5. An oil obtained by heating thallium ethylate with amyl alcohol.

Aluminium amylate $Al(OC_5H_{11})_3$. [70°]. S.G.^{4} ·9801. Formed by action of AlI_3 and iodine (Gladstone a. Tribe, *C. J.* 39, 7; *v.* ALUMINIUM IODIDE, p. 148).

Active amyl alcohol $CEtMeH.CH_2OH$. (128°) (Pedler, *A.* 147, 243); (127°–128°) (Just, *A.* 220, 149). α_D –2·3° (J.); –4·4° (Le Bel; Pierre a. Puchot).

Occurrence.—In fermentation amyl alcohol, which is thus rendered more or less lævorotatory.

Preparation.—Described under inactive amyl alcohol.

Properties.—In a sample for which α was only –1·14°. Perkin (*C. J.* 45, 470) found S.G. $\frac{15}{15}$ ·8150; $\frac{25}{25}$ ·8091; and M.M. 5·94 at 20°. A rotation of more than 4·4° to the left (in a tube 100 mm. long) has been observed by Ley (–11·5°), and by Pedler (–8·6°).

Reactions.—1. A dilute solution mixed with yeast, *penicillium glaucum*, and a little H_2SO_4

becomes dextrorotatory. The new dextrorotatory amyl alcohol forms a lævorotatory iodide (Le Bel, *Bl.* 31, 104).—2. On *oxidation* it yields a dextrorotatory valeric acid, boiling at 170° (Pedler).—3. Hot NaOH renders it inactive.

References.—Pasteur, *C. R.* 41, 296; *A.* 96, 255; Popoff, *B.* 6, 560; Ley, *B.* 6, 1362; Erlenmeyer a. Hell, *A.* 160, 257; Pierre a. Puchot, *C. R.* 76, 1332; Bakhoven, *J. pr.* [2] 8, 272; Le Bel, *B.* 6, 70; 9, 358, 732; *C. R.* 82, 562; *Bl.* 25, 545; Pedler, *A.* 147, 243; Chapman a. Smith, *Pr.* 17, 308.

Methyl-*n*-propyl-carbinol Pr.CMeH.OH (119°). S.G. $\frac{0}{}$ ·824. S. 13·7.

Formation.—1. From its iodide.—2. By reducing methyl propyl ketone with sodium-amalgam (Belohoubek, *B.* 9, 924). So prepared it is inactive, but if it be dissolved in 20 pts. water and *penicillium glaucum* be introduced, it becomes lævorotatory (α −5·5°) (Le Bel, *C. R.* 89, 312).—3. From acetyl chloride and zinc propyl (Markownikoff, *Bl.* [2] 41, 259).

Reactions.—1. *Oxidation* gives methyl propyl ketone.—2. Gives the iodoform reaction.

Methyl-isopropyl-carbinol. Pr.CMeH.OH. (113°). S.G. $\frac{0}{}$ ·833 (Wischnegradsky, *A.* 190, 338).

Formation.—1. From methyl isopropyl ketone with sodium-amalgam (Münch, *A.* 180, 339).—2. By adding water to the product of the action of zinc methide on bromo-acetyl bromide (Winogradoff, *A.* 191, 125), or chloro-acetyl chloride (Bogomoletz, *A.* 209, 86; *Bl.* [2] 34, 330).

Reactions.—1. Conc. H_2SO_4 forms tri-methyl-ethylene, Me_2C:CMeH, which may be converted by warm conc. HI into the iodide of tertiary amyl alcohol.—2. *Oxidation* gives methyl isopropyl ketone, acetone, acetic acid, and CO_2.—3. PCl_5 forms a chloride (87°).

Di-ethyl carbinol Et_2CH.OH. (117°). S.G. $\frac{0}{}$ ·832. Formed by adding water to the product of the action of zinc ethide on ethyl formate (Wagner a. Saytzeff, *A.* 175, 351). The first reaction may be written HCO.OEt + $2ZnEt_2$ = HCEt(OZnEt)Et + ZnEt(OEt). Water then displaces OZnEt by OH. It gives di-ethyl ketone on oxidation.

Tertiary amyl alcohol Et.CMe_2.OH. *Di-methyl-ethyl-carbinol. Amylene hydrate.* [−12°]. (102° cor.) (Perkin, *C. J.* 45, 471). S.G. $\frac{15}{15}$ ·8144; $\frac{25}{25}$ ·8070 (P.). M.M. 5·99 at 19°. H.F.p. 84,510. H.F.v. 81,320 (*Th.*). S.V. 121·3 (R. Schiff, *A.* 220, 102).

Formation.—1. From tertiary amyl iodide (*q. v.*).—2. From zinc methide and propionyl chloride (Popoff, *A.* 145, 292; Jermolajeff, *Z.* 1871, 275; Wyschnegradsky, *A.* 190, 336).

Preparation.—Amylene (1 vol.), prepared from ordinary amyl alcohol, is shaken with an ice-cold mixture of water (1 vol.) and H_2SO_4 (1 vol.).

Reactions.—1. On *oxidation* it gives rise to acetone and acetic acid.—2. When introduced into the stomach (of a rabbit) it is excreted as a glycuronate, $C_{11}H_{20}O_7$, which is split up by acids into the alcohol and glycuronic acid (Thierfelder a. Mering, *H.* 9, 515).—3. Slowly decomposed by *heat* at 220° into H_2O and amylene; this decomposition does not take place unless traces of HCl or HI are present (Wolkoff a. Bougaieff, *J. R.* 1885, 276).

AMYLAMINES $C_5H_{13}N$.

Normal Amylamine

$CH_3.CH_2.CH_2.CH_2.CH_2.NH_2$ (103°).

Formation.—From the amide of normal hexoic acid by the action of bromine and potash (Hofmann, *B.* 15, 770). A mixture of 1 mol. proportion amide and 1 mol. bromine is run into excess of 10 p.c. solution of potash at 60°.

AMYLAMINES FROM AMYL ALCOHOL OF FERMENTATION :—

Ordinary Amylamine

$(CH_3)_2.CH.CH_2.CH_2.NH_2$ (95°–96°). S.G. $\frac{18}{}$ ·7503. S.V. 126·84 (Schiff).

Formation.—1. Amyl cyanate or cyanurate with potash (Wurtz, *A. Ch.* [3] 30, 447; Brazier and Gossleth, *A.* 75, 252).—2. Dry distillation of animal substances (Anderson, *A.* 105, 335).—3. Dry distillation of leucine (Schwanert, *A.* **102**, 225). —4. Amylsulphate of potassium with alcoholic ammonia at 250° (Berthelot, *A.* 87, 372).—5. Distillation of horn with aqueous potash (Limpricht, *A.* 101, 296).—6. Caustic potash on flannel (Gr. Williams, *Chem. Gaz.*, 1858, 310).—7. Amide of isohexoic acid (isobutylacetamide) with bromine and aqueous potash (Hofmann, *B.* 15, 770).—8. In the decomposition of yeast (Müller, *J.* 1857, 403).

Preparation.—Amyl bromide is heated to 100° with alcoholic ammonia in large excess, the alcohol evaporated and the residual hydrobromides decomposed with potash. The oily layer which consists of mono-, di-, and some tri-, amylamine, is dried with caustic baryta and fractionated. Or, potassium amyl sulphate is distilled with potassium cyanate; the resulting amyl cyanate and cyanurate distilled with strong potash; the distillate neutralised with hydric chloride, evaporated and crystallised; and the amylamine obtained by distilling the hydrochloride with lime (Wurtz; Silva, *Bl.* [2] 8, 363).

Properties.—Colourless liquid, miscible with water and alcohol.

Reactions.—1. Oxidised by *chromic acid* to isovaleric acid (Chapman a. Thorpe, *A.* 142, 177).—2. With $ClCO_2Et$ yields ethyl-amyl-carbamate, $C_5H_{11}NHCO_2Et$ (amylurethane) (Custer, *B.* 12, 1329).

Salts.—B'HCl: scales; sol. alcohol.—$B'_2H_2PtCl_6$: scales; sol. hot water, insol. alcohol.—Aurochloride: scales.

Combination.—With *carbonic disulphide* it forms $C^{11}H^{26}N^2S^2(2C^5H^{13}N + CS^2)$ white shining scales, insol. water and ether, sol. alcohol (Hofmann, *C. J.* 13, 60).

Active Amylamine.—The amylamines obtained from active amyl alcohol, probably $(C_2H_5)(CH_3)CH.CH_2OH$ (Erlenmeyer; *v.* AMYL ALCOHOLS; Sauer, *B.* 8, 1037), are optically active, and their salts are much more difficult to crystallise than are those of the corresponding inactive compounds (Plimpton, *C. J.* 39, 332). Amylamine from alcohol rotating 4° for 10 cm. rotated 3° 30′ to the left; (96°–97°); S.G. $\frac{0}{4}$ ·7725.—*Hydrochloride*: deliquescent; feebly dextrogyrate.—*Platino-chloride*: scales; sol. hot water. S. 2·4 at 14°.—*Aurochloride*: sol. alcohol; separates on slow evaporation in lozenge-shaped crystals with the acute angles truncated.

Inactive Amylamine from inactive amyl chloride. (96°–97°). S.G. $\frac{0}{4}$ ·7678; $\frac{11.5}{4}$ ·7501. —*Hydrochloride*: crystallises well.—*Platinochloride* S. 1·7 at 14°: scales.—*Aurochloride*: sol. alcohol; lozenge-shaped crystals with one acute angle truncated.

Diamylamine $(C_5H_{11})_2NH$. (186°–187°). S.G. $\frac{0}{}$ ·7825 (Silva).

Formation.—1. From ord. amylamine and ord. amyl bromide (Hofmann, *A.* 79, 21).—2. From amyl cyanide and potash (Silva, *Z.* 1867, 457). 3. From amyl bromide and alcoholic ammonia (Custer, *B.* 12, 1329; Plimpton, *C. J.* 39, 332; Bell, *B.* 10, 1867).—4. From amyl chloride and aqueous NH_3 at 140°–165° (Mallot, *C. R.* 104, 998).—5. From the nitroso-compound (Custer, *B.* 12, 1333).

Properties.—Oily liquid; sl. sol. water. Reacts with $Cl.CO_2Et$ yielding diamylurethane (Custer).

Salts.—B'HCl: laminæ; crystallises well from hot water.—$(B'HCl)_2PtCl_4$: sol. alcohol, sl. sol. water. Auro-chloride: sol. alcohol, insol. water.

Active Di-amylamine. (182°–184°). S.G. $\frac{0}{4}$ ·7878. From active amyl bromide. (*V.* active amylamine) (Plimpton, *loc. cit.*) Dextrorotatory (5° 15′ for 10 cm.).

Hydrochloride: soluble in water, alcohol, and ether. Much more soluble in cold water than the inactive salt. Solution rotates to the right. *Platinochloride*: sol. alcohol, insol. water. Crystallises from dilute alcohol in octahedrons. *Aurochloride*: insol. water, sol. alcohol.

Inactive Di-amylamine. (186°–187°). S.G. $\frac{0}{4}$ ·7878; $\frac{14}{4}$ ·7776. From inactive amyl chloride (Plimpton).

Hydrochloride: laminæ; rotates when thrown on the surface of water. Insol. ether.—*Platinochloride*: sol. alcohol, insol. water. Crystallises easily from dilute alcohol in rectangular prisms.

Triamylamine $(C_5H_{11})_3N$. (237°). From diamylamine and amyl bromide or from amyl bromide and ammonia (Hofmann, *A.* 79, 22). Amyl cyanate and potash (Silva, *Z.* 1867, 458). Oily liquid, insol. water.

Salts.—B'HCl: crystalline mass with lustre of mother-of-pearl. Platinochloride: rhombic prisms; insol. water, sol. alcohol.

Active Triamylamine. (230°–237°). S.G. $\frac{13}{4}$ ·7964. Prepared from active amyl bromide (3°) and active diamylamine (5° 15′). Rotates 44° 15′ to the right for 10 cm. (Plimpton, *loc. cit.*).

Hydrochloride: syrup which solidifies over sulphuric acid. Solution strongly dextrogyrate.

Aurochloride: needles; insol. water, sol. alcohol.

Inactive Triamylamine. (237°). S.G. $\frac{13}{4}$ ·788. From inactive amyl chloride and ammonia.

Hydrochloride: crystallises from water in prismatic needles, from ether in pearly scales.—*Aurochloride*: needles; sol. alcohol. Inactive triamylamine may be separated from inactive diamylamine by treating the hydrochlorides with ether which dissolves the triamylamine salt.

Tetramylammonium Salts.

Iodide $(C_5H_{11})_4NI$. From ordinary amyl iodide and triamylamine or amyl iodide and ammonia (Hofmann, *C. J.* 4, 316). The mixture of triamylamine and amyl iodide is boiled and after three or four days solidifies on cooling into an unctuous crystalline mass. Monoclinic laminæ (Lang, *J.* 1867, 491). Dissolves sparingly in water forming an extremely bitter solution from which it is ppd. in a crystalline form by alkalis. Boiled with silver oxide it yields a very bitter alkaline solution of *Tetramylammonium hydroxide.* On mixing the liquid with potash or on concentrating, the hydroxide separates as an oily layer, which gradually solidifies. By evaporating a solution of the hydroxide in an atmosphere free from carbonic acid, crystals containing several molecules of water are obtained. When heated these crystals melt and give off water, triamylamine, and a hydrocarbon which is probably amylene.

$(C_5H_{11})_4NCl$: laminæ with palm-like ramifications. — $((C_5H_{11})_4NCl)_2PtCl_4$: orange-yellow needles.—*Sulphate*: long capillary threads.—*Nitrate*: needles. — *Oxalate*: large deliquescent plates.

Amylamine. Corresponding to methyl propyl carbinol. $(CH_3)(C_3H_7)CHNH_2$. (89°–91°). By reduction of methyl propyl ketone phenyl hydrazide in alcoholic solution with sodium amalgam and acetic acid (Tafel, *B.* 19, 1924). Mobile liquid, smelling strongly ammoniacal, miscible with water, alcohol, and ether.

Hydrochloride: silky needles. — *Platinochloride*: yellow needles; sol. water and hot alcohol, less so in cold alcohol.—*Oxalate*: crystallises from hot alcohol in scales.

Tertiary amylamine. $(CH_3)_2(C_2H_5)CNH_2$. (77·5°–78°). S.G. $\frac{0}{}$ ·7611; $\frac{15.5}{}$ ·7475. Formerly considered to be $(CH_3)_2CH(CH_3)CHNH_2$ on account of its formation from the cyanate corresponding to Wurtz's amylene hydriodide and amylene hydrate, then regarded as isopropyl-methyl carbinol, and now shown to be dimethyl-ethyl carbinol (Flavitzky, *A.* 179, 310).

Formation.—1. From pseudoamylurea and strong potash (Wurtz, *Bl.* [2] 7, 143).—2. By the action of dimethyl ethyl carbinol iodide on the cyanides of potassium and mercury, and treatment of the nitrile so obtained with hydric chloride (Wyschnegradsky, *A.* 174, 60).—3. By treating the product of the action of the same iodide upon silver cyanate with strong hydric chloride (Rudnew).

Properties.—Odour ammoniacal; pps. copper salts but does not redissolve the ppd. cupric hydrate.

Hydrochloride: efflorescent scales, or octahedrons, from alcohol and ether. — *Platinochloride*: fine crystals derived from a monoclinic prism, easily soluble water and alcohol. — *Aurochloride*: large yellow crystals, monoclinic.

Reactions. — With bromine it forms bromamyl-amine $C_5H_{12}BrN$ which can be distilled with steam (Wurtz). R. T. P.

AMYL-ANILINE $C_{11}H_{17}N$ *i.e.* $C_6H_5.NHC_5H_{11}$. (258°). Mol. w. 163. From aniline and isoamyl bromide (Hofmann, *C. J.* 3, 297). Smells, when cold, like roses. When its hydrochloride is

heated at 320° it changes to the hydrochloride of amido-phenyl-pentane, $C_5H_{11}.C_6H_4.NH_2$ (Hofmann, *B.* 7, 529).

Isoamyl-aniline $C_6H_5.NHC_5H_{11}$ (243°) at 720 mm. Colourless oil. V. sol. alcohol, ether, and benzene, insol. water. Is a by-product of the action of isovaleric aldehyde and HCl upon aniline. Salts.—B'HCl: colourless prisms, v. sol. water. The nitrate and oxalate are sparingly soluble. The picrate is a reddish-yellow oil.

Acetyl derivative $C_6H_5.N(C_5H_{11})Ac$, (278°) at 720 mm., colourless fluid, v. sol. alcohol and ether; insol. water.

Nitrosamine $C_6H_5.N(C_5H_{11})NO$: oil; volatile with steam; v. sol. alcohol and ether, insol. water (Spady, *B.* 18, 3376).

Di - isoamyl - aniline $C_6H_5N(C_5H_{11})_2$. (275°–280°) (Hofmann, *A.* 74, 156). —$B'_2H_2PtCl_6$.

Iso - **AMYL - ANTHRACENE** $C_{19}H_{20}$ *i.e.* $C_6H_4\Big<\begin{matrix}C(C_5H_{11})\\|\\CH\end{matrix}\Big>C_6H_4$. [59°]. From amyl-hydro-anthranol by boiling alcoholic HCl.

Preparation.—Anthraquinone (30 g.), zinc dust (100 g.) NaOH (50 g.), water (450 g.) are boiled together for 5 hours and then amyl bromide is added. The liquid is poured off, and the pp. dissolved in alcohol, reppd. by water, and boiled with alcoholic HCl (Liebermann, *A.* 212, 104; *B.* 14, 796).

Properties.—Long sea-green needles with blue fluorescence (from alcohol). Conc. H_2SO_4 gives a green solution. V. sol. benzene, CS_2, chloroform, or benzoline. *Picrate* forms red needles [115°], CrO_3 in HOAc gives amyl-oxanthranol. Forms a *bromo compound* $C_6H_4<\begin{matrix}C(C_5H_{11})\\CBr\end{matrix}>C_6H_4$. [76°]. Picrate [110°]. Forms also a corresponding *chloro-derivative* [71°]. Picrate [108°].

Iso-**Amyl-anthracene-di-hydride** $C_{19}H_{22}$ *i.e.* $C_6H_4<\begin{matrix}CH(C_5H_{11})\\CH_2\end{matrix}>C_6H_4$. (350°); (292°) at 570 mm. S.G. $\frac{18}{18}$ 1·031. Prepared by reduction of amyl-oxanthranol with P and HI (Liebermann, *B.* 14, 457; 15, 1000; *A.* 212, 79). Clear fluorescent liquid. Miscible with alcohol, ether, benzene, and acetic acid, in all proportions. On oxidation with HNO_3 anthraquinone is formed.

Iso-**AMYL ARSENATE** $(C_5H_{11})_3AsO_4$ (Crafts, *Bl.* 14, 101).

Iso-**AMYL ARSENITE** $(C_5H_{11})_3AsO_3$. (288°) (Crafts, *Bl.* 14, 105).

n-**AMYL-BENZENE.** *Phenyl-pentane.* $C_{11}H_{16}$ *i.e.* $Ph.CH_2.CH_2.CH_2.CH_2.CH_3$. Mol. w. 148. (201° uncor.) at 743 mm. S.G. $\frac{22}{}$ ·8602. From benzyl bromide, *n*-butyl bromide, and sodium (Schramm, *A.* 218, 388). Pleasant smelling oil.

Reaction.—Bromine vapour at 150° gives $Ph.CHBr.CH_2.CH_2.CH_2.CH_3$ (?) which on distillation gives $Ph.CH:CH.CH_2.CH_2.CH_3$ (210°–215°) which combines with Br_2 forming $Ph.CHBr.CHBr.CH_2.CH_2.CH_3$. [54°].

Isoamyl-benzene (193°) at 736 mm. S.G. $\frac{12}{}$ ·859. From bromo-benzene, isoamyl bromide, and Na (Fittig a. Tollens, *A.* 129, 369; 131, 313; Bigot a. Fittig, *A.* 141, 160; Schramm, *A.* 218, 390). Also from isoamyl chloride, benzene, and $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 1, 454).

Reaction.—Bromine vapour at 150° gives $Ph.CHBr.CH_2.CH(CH_3)_2$(?) which on distillation gives HBr and $Ph.CH:CH.CH(CH_3)_2$, phenyl-isoamylene, which forms a dibromide [129°].

Di-ethyl-carbinyl-benzene $Ph.CHEt_2$. (178°). S.G. $\frac{21}{}$ ·873.

Formation.—1. From benzylidene chloride and zinc ethide (Lippmann a. Luginin, *Z.* 1867, 674).—2. From benzo-trichloride, $Ph.CCl_3$, and zinc ethide (Dafert, *M.* 4, 153, 616).

Tert-**amyl-benzene** $Ph.CMe_2Et$. (c. 187°). S.G. $\frac{0}{}$ ·874. From tert-amyl chloride, benzene, and $AlCl_3$ (Essner, *Bl.* [2] 36, 212).

Di-isoamyl-benzene $C_{16}H_{26}$ *i.e.* $(C_5H_{11})_2C_6H_4$. (c. 265°). S.G. $\frac{0}{}$ ·887. From benzene, isoamyl chloride, and $AlCl_3$ (Austin, *Bl.* [2] 32, 12).

AMYL-BENZENE SULPHONIC ACIDS $C_{11}H_{16}SO_3$ *i.e.* $C_5H_{11}.C_6H_4SO_3H$.

Isoamyl-benzene sulphonic acid. Deliquescent crystalline mass (Fittig a. Tollens, *A.* 131, 315). Salts.—KA' aq.—BaA'_2: hair-like needles.

Di-ethyl-carbinyl-benzene sulphonic acid $CHEt_2.C_6H_4.SO_3H$. Salts.—BaA'_2 1½aq: pearly leaflets, sl. sol. water and alcohol (Dafert, *M.* 4, 617).

p-*Iso*-**AMYL-BENZOIC ACID** $C_{12}H_{16}O_2$ *i.e.* $C_6H_4(C_5H_{11}).CO_2H$ [1:4] [158°]. Formed by saponification of the nitrile. Sublimes in flat colourless needles. Sol. alcohol, ether, and hot water, sl. sol. cold water. Salt: AgA': small colourless needles, sl. sol. cold water (Kreysler, *B.* 18, 1710).

p-*Iso*-**AMYL-BENZONITRILE** $C_6H_4(C_5H_{11}).CN$ (260°–263° uncorr.). Colourless oil. Formed by heating tri-isoamylphenyl-phosphate with dry KCN; yield—20 p.c. (Kreysler, *B.* 18, 1709).

Iso - **AMYL BORATE** $C_{15}H_{33}BO_3$ *i.e.* $(C_5H_{11}O)_3B$. (254°). S.G. $\frac{0}{}$ ·872.

Iso-amyl borate $(C_5H_{11}O)BO$. S.G. $\frac{0}{}$ ·971. Oil.

n-**AMYL BROMIDE** $C_5H_{11}Br$ *i.e.* $CH_3.CH_2.CH_2.CH_2.CH_2Br$. Mol. w. 151. (129°). S.G. $\frac{0}{}$ 1·246. From *n*-amyl alcohol (Lieben a. Rossi, *A.* 159, 73).

Inactive amyl bromide $(CH_3)_2CH.CH_2.CH_2Br$ (120·6° i. V.) at 734 mm. S.G. $\frac{22}{}$ 1·026 (Lachowicz, *A.* 220, 171).

Isoamyl bromide (118·5°) at 756 mm. (R. Schiff, *B.* 19, 563). H.F.p. 34,000 (Berthelot). S.V. 138·6 (S.); 143·8 (Ramsay). For a specimen which rotated + ·52° in 100 mm. Perkin (*C. J.* 45, 458) found: (120·5° cor.); S.G. $\frac{15}{15}$ 1·2193; $\frac{25}{25}$ 1·2083; M.M. 9·01 at 17°.

Active amyl bromide (117°–120°); S.G. $\frac{15}{}$ 1·225 (Le Bel, *Bl.* [2] 25, 545). Dextrorotatory; $\alpha = +3·75°$.

n-*Sec*-**amyl bromide** $CH_3.CH_2.CH_2.CHBr.CH_3$. (113°) (Wurtz, *A.* 125, 118). Formed when isoamyl bromide is heated at 230° (Eltekow, *B.* 8, 1244).

Iso-*sec*-**amyl bromide** $(CH_3)_2CH.CHBr.CH_3$. (116°) (Wyschnegradsky, *A.* 190, 357).

Tert-**amyl bromide** $CH_3.CH_2.CBr(CH_3)_2$. (109°).

AMYL-BROMO- *v.* BROMO-AMYL.

Iso-**AMYL-CARBAMIC ETHER** $C_8H_{17}NO_2$ *i.e.* $C_5H_{11}NHCO_2Et$. *Amyl-urethane.* (218°). S.G. ·93. From isoamyl-amine and $ClCO_2Et$ (Custer, *B.* 12, 1328). Oil; sol. alcohol and ether.

Di-isoamyl-carbamic ether $(C_5H_{11})_2N.CO_2Et$. (247°). From di-isoamyl-amine and $ClCO_2Et$ (C.).

***Iso*-AMYL CARBAMINE** $C_6H_{11}N$ *i.e.* $C_5H_{11}NC$. (187°). Mol. w. 97 (Hofmann, *A.* 146, 109).

***Iso*-AMYL CARBONATE** $C_{11}H_{22}O_3$ *i.e.* $(C_5H_{11})_2CO_3$ (229° cor.). S.G. $\frac{15}{}$ ·91.

***Iso*-AMYL CETYL OXIDE** $C_{21}H_{44}O$ *i.e.* $C_5H_{11}OC_{16}H_{33}$. [30°]. Plates.

***n*-AMYL CHLORIDE** $C_5H_{11}Cl$ *i.e.* $CH_3.CH_2.CH_2.CH_2.CH_2Cl$. Mol. w. 106·5. (106°). S.G. $\frac{20}{}$ ·873 (Lachowicz, *A.* 220, 191); ·883 (L. a. R.). Formed from *n*-amyl alcohol (Lieben a. Rossi, *A.* 159, 72; *G.* 1, 314) or by the chlorination of *n*-pentane (Schorlemmer, *A.* 161, 268).

Inactive amyl chloride $(CH_3)_2CH.CH_2.CH_2Cl$. (99·8°-100·5°). S.G. $\frac{20}{}$ ·870. From iso-pentane (Lachowitz).

Iso-amyl chloride (99·5°) (R. Schiff, *B.* 19, 562). S.V. 134·4 (S.); 136·5 (Ramsay). In a specimen which rotated +5·8° in 100 mm. Perkin (*C. J.* 45, 452) found: (97°-99° cor.); S.G. $\frac{15}{15}$ ·8801; $\frac{25}{25}$ ·8716; M.M. 7·17 at 19·5°.

Formation.—1. From isoamyl alcohol and HCl (Balard, *A. Ch.* [3] 12, 294), S_2Cl_2 (Carius a. Fries, *A.* 109, 1), or PCl_5 (Cahours, *A.* 37, 164).

Reactions.—1. Converted into amyl alcohol by water at 100° (Butlerow, *A.* 144, 34), or better at 120° (Niederist, *A.* 186, 392).—2. H_2SO_4 forms HCl and $C_5H_{11}SO_4H$ (Oppenheim, *J. pr.* 102, 339).

Active amyl chloride $CH_3.CH_2.CH(CH_3).CH_2Cl$. (99°). $a = +1·24°$. S.G. $\frac{15}{}$ ·886 (Le Bel, *Bl.* [2] 25, 546).

***n-Sec*-amyl chloride** $CH_3.CH_2.CH_2.CHCl.CH_3$. (104°). S.G. $\frac{21}{}$ ·891. From *n*-pentane by chlorination (Schorlemmer; Lachowicz). From $CH_3.CH_2.CH:CH.CH_3$ and HCl (Wagner a. Saytzeff, *A.* 179, 321).

***Iso-sec*-amyl chloride** $(CH_3)_2CH.CHCl.CH_3$. (91°). S.G. $\frac{0}{}$ ·88. From $(CH_3)_2CH.CH:CH_2$ and HCl (Berthelot, *C. R.* 56, 700; Wurtz, *A.* 129, 368; Wyschnegradsky, *A.* 190, 357).

***s-Sec*-amyl chloride** Et_2CHCl. (103°-105°). S.G. $\frac{21}{}$ ·895. From the alcohol (W. a. S.).

***Tert*-amyl chloride** $EtCMe_2Cl$. (86°). S.G. $\frac{19}{}$ ·870. By action of PCl_5 on tert-amyl alcohol or on methyl-isopropyl-carbinol (Wyschnegradsky, *A.* 190, 336; 191, 331).

AMYL-CHLORO- *v.* CHLORO-AMYL.

***Iso*-AMYL CYANATE** $C_6H_{11}NO$ *i.e.* $C_5H_{11}N.CO$. (135°). Prepared by distilling amyl-carbamic ether with P_2O_5 (Custer, *B.* 12, 1330), or from $C_5H_{11}SO_4K$ and potassium cyanate (Wurtz, *A. Ch.* [3] 42, 43). With *ammonia* it yields amyl-urea, and with *potash* it yields amylamine.

AMYL CYANIDE *v.* AMYL CARBAMINE and nitrile of HEXOIC ACID.

AMYLENE C_5H_{10}. *Pentene.* Mol. w. 70.

***n*-Propyl-ethylene** $CH_3.CH_2.CH_2.CH:CH_2$. (40°).

Formation.—1. Together with amyl acetate when KOAc and Ac_2O act on *n*-amyl chloride at 200° (Schorlemmer, *A.* 161, 269).—2. Together with di-allyl (principal product), pentane, and other bodies, in the action of zinc ethide on allyl iodide (Wurtz, *A.* 123, 203; 127, 55; 148, 131).

Properties.—Liquid; insol. H_2SO_4 (2 vols.) diluted with water (1 vol.).

Reactions.—1. Gives Pr.CHI.Me with HI.—2. Alkaline $KMnO_4$ gives succinic, butyric, oxalic, and formic acids (Zeidler, *A.* 197. 253).

Isopropyl-ethylene $(CH_3)_2CH.CH:CH_2$. (21°). Formed together with $EtCMe:CH_2$ by action of alcoholic KOH on isoamyl iodide (Wyschnegradsky, *B.* 10, 81; *A.* 190, 328).

Properties.—Liquid; insol. at 0° in H_2SO_4 (2 vols.) mixed with water (1 vol.).

Reactions.—Does not combine with HI at −20°, but at 20° it combines slowly forming $(CH_3)_2CH.CHI.CH_3$.

***s*-Methyl-ethyl-ethylene** $CH_3.CH:CH.Et$. (36°).

Formation.—1. From $CH_3.CH_2.CHI.CH_2.CH_3$ (Wagner a. Saytzeff, *A.* 175, 373; 179, 302), or $CH_3.CHI.CH_2.CH_2.CH_3$ (Wurtz), and an alcoholic solution of KOH.—2. From ethyl-crotonic acid, $CH_3.CH:CEt.CO_2H$, by combining it with HBr and neutralising the resulting β-bromo-di-ethyl-acetic acid: $CH_3.CHBr.CEtH.CO_2Na = NaBr + CO_2 + CH_3.CH:CEtH$ (Fittig, *A.* 200, 27).

Reaction.—HI forms $CH_3.CHI.CH_2.CH_2.CH_3$.

***u*-Methyl-ethyl-ethylene** $Et.C(CH_3):CH_2$. (32°). S.G. $\frac{0}{}$ ·670. From active amyl iodide and alcoholic KOH (Le Bel, *Bl.* [2] 25, 546).

Properties.—Liquid; dissolves in H_2SO_4 (2 vols.) diluted with water (1 vol.).

Reactions.—HI forms $CH_3.CH_2.CI(CH_3).CH_3$.

Tri-methyl-ethylene $(CH_3)_2C:CH.CH_3$. (36°). S.G. $\frac{15}{15}$ ·6704; $\frac{25}{25}$ ·6614. M.M. 6·121 at 13·2° (Perkin, *C. J.* 45, 448).

Formation.—1. From $CH_3.CH_2.CI(CH_3)_2$ (Ermolajeff, *Z.* [2] 6, 275) or $CH_3.CHI.CH(CH_3)_2$ (Wy.) and alcoholic KOH.—2. From ethyl isoamyl oxide and P_2O_5 (Flavitzky, *A.* 169, 206).

Properties.—Liquid; soluble at 0° in H_2SO_4 (2 vols.) diluted with water (1 vol.)

Reaction.—HI forms $(CH_3)_2CI.CH_2.CH_3$.

Iso-amylene. (36°). S.G. $\frac{9·9}{4}$ ·661; $\frac{20}{4}$ ·648. H.F.p. 10,600 (Berthelot); 18,970 (*Th.*). H.F.v. 16,650 (*Th.*). V.D. 2·47 (for 2·42). S.V. 110 (R. Schiff, *A.* 220, 89); 110·8 (Ramsay). μ_β 1·3813. R_∞ 39·29 (Brühl). A mixture of tri-methyl-ethylene (90 p.c.) and *u*-methyl-ethyl ethylene (10 p.c.) with a small quantity of isopropyl-ethylene (Flavitzky, *A.* 179, 340).

Preparation.—From isoamyl alcohol and $ZnCl_2$, many other hydrocarbons being also formed (Etard, *C. R.* 86, 488; Wyschnegradsky, *C. R.* 86, 973).

Properties.—Absorbed at 0° by H_2SO_4 (2 vols.) diluted with water (1 vol.), with production of tertiary amyl alcohol. A more dilute acid (2 pts. H_2SO_4 to 1 pt. water by weight) forms methyl-isopropyl-carbinol (Ossipoff, *B.* 8, 542, 1240).—NOCl forms a compound $C_5H_{10}NOCl$ which may be reduced to amylamine (Tönnies, *B.* 12, 169).—3. $C_5H_{10}K_2PtCl_4aq$ is formed by boiling isoamyl alcohol with $PtCl_4$ and then adding KCl (Birnbaum, *A.* 145, 73); deliquescent plates.

Other References.—Balard, *A. Ch.* [3] 12, 320; Frankland, *C. J.* 3, 35; Bauer, *Sitz. B.* 44 [2] 87; *Z.* 1866, 380, 667; Bauer a. Klein, *Z.* [2] 4, 386; Guthrie, *A.* 121, 108; Lippmann, *A.* 129, 81; *M.* 5, 559; Eltekoff, *B.* 6, 1258; Linnemann, *A.* 143, 350; Buff, *A. Suppl.* 4, 143; 148, 349; Thorpe a. Young, *A.* 165, 7; Flavitzky, *A.* 165, 157; Le Bel, *Bl.* 17, 3; 18, 166; Berthelot, *A. Ch.* [4] 9, 442; *C. R.* 44, 1350; Renard, *A. Ch.* [6] 1, 227; Markownikoff, *Z.* [2] 2, 502.

Oxidation of amylenes.—Examined by Zeid-

ler, *A.* 186, 245; 197, 258; Truchot, *C. R.* 63, 274; Berthelot, *C. R.* 64, 86.

Di-amylene $C_{10}H_{20}$. (156°). S.G. $\frac{19}{4}$ ·780. R_{∞} 76·58 (Nasini a. Bernheimer, *G.* 15, 93). S.V. 211·18. Occurs in the product of action of $ZnCl_2$, H_2SO_4, or P_2O_5, on isoamyl alcohol; and is also formed by shaking amylene with H_2SO_4.

Reactions.—1. *Bromine* forms $C_{10}H_{20}Br_2$.—2. *Chromic acid mixture* produces *amethenic acid* $C_7H_{14}O_2$ (Schneider, *A.* 157, 213; Pawlow, *J. R.* 9, 75).

Combinations.—$C_{10}H_{20}S_2Cl_2$; from amylene and S_2Cl_2 (Guthrie, *C. J.* 12, 112; 13, 35; 14, 128). Distilled over KOH it forms $C_{10}H_{18}S_2$, (112°), S.G. $\frac{13}{}$ ·880. $ZnEt_2$ gives $C_{14}H_{30}S_2$ (240°–250°).

References.—Balard, *A. Ch.* [3] 12, 320; Bauer, *Bl.* 1863, 332; 1867, 341; Berthelot, *C. R.* 56, 1242; Walz, *Z.* [2] 4, 315; W. v. Schneider, *A.* 157, 185; Wyschnegradsky, *B.* 8, 434; Lebedeff, *J. R.* 7, 246; Tugolessoff, *B.* 12, 1486.

Triamylene $C_{15}H_{30}$. (248°). S.G. ·81. V.D. 7·6 (for 7·4). Among products of action of $ZnCl_2$ on isoamyl alcohol (Bauer, *Sitz. B.* 44 [2] 87; *A.* 137, 249; 147, 254). Forms a bromide, $C_{15}H_{30}Br_2$, converted by alcoholic KOH into benylene, $C_{15}H_{28}$, (223°–228°).

Tetra-amylene $C_{20}H_{40}$. (390°–400°). S.G. $\frac{0}{}$ ·871. Among products of action of $ZnCl_2$ on isoamyl alcohol (Balard; Bauer).

AMYLENE DI-ACETIN *v. di*-OXY-PENTANE.

AMYLENE BENZOATE *v. di*-OXY-PENTANE.

AMYLENE BROMIDE *v. di*-BROMO-PROPANE.

AMYLENE TRI-CARBOXYLIC ACID $C_8H_{10}O_6$ *i.e.* $CH_2{:}CH.CH_2.C(CO_2H)_2.CH_2.CO_2H$.

Ether.—Et_3A'''. [151°]. Obtained by introducing allyl into ethane tri-carboxylic acid (Hjelt, *B.* 16, 333). At 160° it splits up into CO_2 and allyl-succinic acid (*q. v.*).

AMYLENE CHLORHYDRIN *v.* CHLORO-AMYL ALCOHOL.

AMYLENE CHLORIDE *v. di*-CHLORO-PENTANE.

AMYLENE-CHLORO-SULPHIDE *v. di*-AMYLENE, *Combinations.*

AMYLENE IS-ETHIONIC ACID *v.* OXY-PENTANE SULPHONIC ACID.

AMYLENE GLYCOL *v. di*-OXY-PENTANE.

AMYLENE GUANAMINE $C_8H_{15}N_5$. [178°]. Formed by heating guanidine caproate (hexoate) at 225° (Bandrowski, *B.* 9, 243). Crystals; v. sl. sol. water, v. sol. alcohol. Salt.—B'HCl.

AMYLENE HYDRATE. Tertiary AMYL ALCOHOL (*q. v.*).

AMYLENE HYDRIDE. PENTANE (*q. v.*).

AMYLENE HYDROCHLORIDE. AMYL CHLORIDE (*q. v.*).

AMYLENE NITRITE $C_5H_{10}N_2O_4$ *i.e.* $C_5H_{10}(NO_2)_2$. From amylene by treatment with NO_2 or fuming HNO_3 (Guthrie, *C. J.* 13, 45, 129). Tables; decomposed at 95°.

AMYLENE OXIDE $C_5H_{10}O$.

Isopropyl-ethylene oxide $Pr.CH\left<\begin{array}{l}O\\ |\\ CH_2\end{array}\right.$ (82°). By action of potash on chloro-amyl alcohol, $Pr.CHCl.CH_2OH$ or $PrCH(OH).CH_2Cl$ (Eltekoff, *Bl.* [2] 40, 23; *J. R.* 14, 355). Heated with water for 50 hours at 100° it forms $Pr.CH(OH).CH_2OH$. Does not combine with $NaHSO_3$.

Tri-methyl-ethylene oxide $Me_2C\left<\begin{array}{l}O\\ |\\ CHMe\end{array}\right.$ (76°). S.G. $\frac{0}{}$ ·829.

Preparation.—By action of potash on the chloro-amyl alcohol obtained by the union of $Me_2C{:}CHMe$ with HClO (E.).

Properties. — Liquid; readily unites with cold water to form di-oxy-pentane. Does not combine with $NaHSO_3$.

Methyl-ethyl-ethylene oxide $MeCH\left<\begin{array}{l}O\\ |\\ CHEt\end{array}\right.$ (80°). Prepared by action of potash on the chloro-amyl alcohol resulting from union of $Me.CH{:}CHEt$ with HClO (E.). Unites at 100° with water forming $MeCH(OH).CHEt(OH)$.

Di-amylene oxide $C_{10}H_{20}O$. (170°–180°). From di-acetyl-di-OXY-DECANE (*q. v.*) (di-amylene di-acetin) and solid KOH (Bauer, *Sitz. B.* 45, 276) Oil. Reduces ammoniacal $AgNO_3$.

Di-amylene oxide (198°–203°). V.D. 5·3 (for 5·4). Obtained as an oil by the action of potash on a mixture of amylene and Bz_2O_2 that has been heated at 110° (Lippmann, *M.* 5, 562). Does not reduce ammoniacal $AgNO_3$ or combine with $NaHSO_3$.

Di-amylene oxide (180°–190°). From di-amylene and chromic mixture (Schneider, *A.* 157, 221). Reduces ammoniacal $AgNO_3$. Oxidised to amethenic acid, $C_7H_{14}O_2$.

Di-amylene oxide (193°). From di-amylene bromide (*v. di*-BROMO-DECANE), water, and PbO (Eltekoff, *J.* 1878, 374).

Two or more of the preceding di-amylene oxides may be identical.

AMYLENE SULPHIDE $C_5H_{10}S$. (c. 200°). S.G. $\frac{13}{}$ ·907. Formed by boiling $C_{10}H_{20}S_2Cl_2$ (*v.* DIAMYLENE) with zinc (Guthrie, *C. J.* 14, 128). Colourless oil.

Amylene sulphide (?) $C_5H_{10}S$. (130°–150°). V.D. 3·2 (calc. 3·5). Formed by action of acids or of heat upon the product of the union of $ZnEt_2$ and CS_2 (Grabowsky, *A.* 138, 165). Alcoholic $HgCl_2$ forms plates of $C_5H_{10}S\,HgS\,HgCl_2$; alcoholic $AgNO_3$ forms $C_5H_{10}OAg_2OAgNO_3$.

AMYL ENNONYL KETONE (?) $C_{15}H_{24}O$ *i.e.* $Et_2CH.CO.C_6H_4(C_2H_5)_3$ (?). (280°–300°). One of the products got by passing CO over a mixture of NaOEt and NaOAc at 250° (Geuther a. Fröhlich, *A.* 202, 312).

AMYL ENNYL KETONE $C_{14}H_{28}O$ *i.e.* $C_4H_9.CO.C_9H_{19}$ (?). *Amyl-valerone.* (209°). S.G. $\frac{12}{}$ ·845. One of the products of the passage of CO over sodium iso-amylate at 100° (Geuther a. Fröhlich, *A.* 202, 301). Liquid; smells like quinces. Does not combine with $NaHSO_3$.

AMYL ETHER *v.* AMYL OXIDE.

AMYL FLUORIDE $C_5H_{11}F$. (72°–92°). A mixture of amyl fluoride and polymerides of amylene is formed by saturating amylene at 0° with HF (S. Young, *C. J.* 39, 489).

AMYL-GLYOXALINE $C_8H_{14}N_2$ *i.e.* $CH\left<\begin{array}{l}NH\\ CH.N\end{array}\right>C.C_5H_{11}$ (?). *Glyoxal-œnanthyline.* [84°]. From œnanthol-ammonia and glyoxal (Radziszewski, *B.* 16, 748). Thin glistening needles. Sol. alcohol, sl. sol. ether, insol. water.

Iso-amyl-glyoxaline $C_8H_{14}N_2$ *i.e.* $CH\langle{}^{N(C_5H_{11})}_{CH-N}\rangle CH$ (?). (240°–245°).

S.G. ¹² ·94. From glyoxaline and amyl bromide (Wallach, *A.* 214, 322; *B.* 15, 651). Liquid; v. sl. sol. water, sol. even in very dilute alcohol.

Salt.—$B'_2H_2PtCl_6$: plates (from alcoholic HCl); v. sl. sol. cold water or cold alcohol.

Iso-**AMYL HEPTYL OXIDE** $C_{12}H_{26}O$ *i.e.* $C_5H_{11}.O.C_7H_{15}$. *Amyl-œnanthyl ether.* (221°). S.G. $\frac{20}{}$ ·668. V.D. 6·57 (calc. 6·45). From sodium heptylate and isoamyl iodide (Wills, *C. J.* 6, 316).

(*Py.* 2:3)-**AMYL-HEXYL-QUINOLINE**

$C_{20}H_{29}N$ *i.e.* $C_6H_4\langle{}^{CH:C(C_5H_{11})}_{N:C(C_6H_{13})}$. (320°–360°).

Oily fluid. Formed by the action of œnanthic aldehyde and HCl upon aniline (Doebner a. Miller, *B.* 17, 1719).

Salts.—$B'_2H_2Cl_2PtCl_4$: large yellow plates. —$B'C_6H_2(NO_2)_3OH$: yellow needles; sl. sol. water and cold alcohol.

AMYL HYDRIDE *v.* PENTANE.

Iso-**AMYL-HYDRO-ANTHRANOL** $C_{19}H_{22}O$ or $C_6H_4\langle{}^{C(C_5H_{11})(OH)}_{CH_2}\rangle C_6H_4$. [74°]. Formed, as a by-product in the treatment of anthraquinone with zinc-dust and amyl bromide (Liebermann a. Tobias, *B.* 14, 801; *A.* 212, 102). Crystalline solid. Insoluble in water, extremely soluble in other solvents. On boiling with alcoholic HCl it gives amyl-anthracene.

Iso-**AMYL-HYDROQUINONE.** From iso-amyl-arbutin and dilute H_2SO_4, glucose being also formed (Schiff a. Pellizzari, *A.* 221, 365). Needles. Gives a crystalline nitro-derivative.

AMYLIDENE-ACETO-ACETIC ETHER *v.* p. 24.

Iso-**AMYLIDENE-*m*-AMIDO-BENZOIC ACID** $C_{12}H_{15}NO_2$ *i.e.* $C_4H_9.CH:N.C_6H_4.CO_2H$. [c. 130°]. From valeric aldehyde and *m*-amido-benzoic acid (Schiff, *A.* 210, 119).

AMYLIDENE ANILINE $C_{11}H_{15}N$ *i.e.* $Me_2CH.CH_2.CH:NPh$. [97°]. From valeric aldehyde and aniline in the cold (Lippmann a. Strecker, *B.* 12, 74). Prisms. — B'HCl. — $B'_2H_2PtCl_6$. Valeric aldehyde and aniline at 100° form di-amylidene-di-phenyl-diamine, a neutral oil, $C_{22}H_{30}N_2$ (Schiff, *B.* 12, 298).

AMYLIDENE BIURET $C_7H_{13}N_3O_2$. From valeric aldehyde and cyanic acid (Baeyer, *A.* 114, 164).

AMYLIDENE BROMIDE *v.* *di*-BROMO-PENTANE.

AMYLIDENE-DI-CARBAMIC ETHER $C_{11}H_{22}N_2O_4$ *i.e.* $Me_2CH.CH_2.CH(NH.CO_2Et)_2$. *Amylidene urethane.* [126°] From carbamic ether, valeric aldehyde, and conc. HCl (Bischoff, *B.* 7, 633). Needles. Split up by hot dilute acids into valeric aldehyde and carbamic ether.

AMYLIDENE CHLORIDE *v.* *di*-CHLORO-PENTANE.

α **AMYLIDENE GLYCOL** *v.* *ortho*-VALERIC ALDEHYDE.

AMYL IODIDES $C_5H_{11}I$. Mol. w. 198.

n-**Amyl iodide** $CH_3.CH_2.CH_2.CH_2.CH_2I$. (156° cor.) S.G. $\frac{0}{}$ 1·544; $\frac{20}{}$ 1·517. From the chloride and HI (Lieben a. Rossi, *A.* 159, 74).

Iso-**amyl iodide.** (148°). S.G. $\frac{15}{15}$ 1·510; $\frac{15}{15}$ 1·498. M.M. 13·20 at 19·6° (Perkin, *C. J.* 45, 482). S.V. 151·08 (R. Schiff, *B.* 19, 564). From isoamyl alcohol (4 pts.), iodine (5 pts.), and P (Cahours, *A. Ch.* [2] 70, 81; Grimm, *J. pr.* 62, 385). From amyl-chloride and $CaI_2 3\frac{1}{2}aq$ at 100° (Van Romburgh, *R.* 1, 151). Partially converted by heating with EtOH into EtI and isoamyl alcohol (Friedel a. Crafts, *A.* 130, 198).

Active amyl iodide $EtCHMe.CH_2I$. (144°–145°). S.G. $\frac{10}{10}$ 1·5425 (Just, *A.* 220, 152). α = 3·76° for 100 mm. at 16° (J.); 5·2° (Le Bel, *Bl.* [2] 25, 542). From the alcohol by HI. Reduced in alcoholic solution by Sn and conc. HCl. to inactive isopentane (J.)

n-n-Sec-**amyl iodide** $CH_3.CH_2.CH_2.CHI.CH_3$. (144°–145°). S.G. $\frac{0}{}$ 1·539. Formed by union of HI with $CH_3.CH_2.CH_2CH:CH_2$ (Wagner a. Saytzeff, *A.* 179, 313; Wyschnegradsky, *A.* 190, 347) or $CH_3.CH_2.CH:CH.CH_3$ (Wurtz, *A.* 148, 132).

Iso-sec-**amyl iodide** $(CH_3)_2CH.CHI.CH_3$. (137°–139°). From $(CH_3)_2CH.CH:CH_2$ and HI (Wy.). Water and PbO convert it into $(CH_3)_2C(OH).CH_2.CH_3$.

s-n-Sec-**amyl iodide** $CH_3.CH_2.CHI.CH_2.CH_3$. (145°–146°). S.G. $\frac{0}{}$ 1·528; $\frac{20}{}$ 1·50. From di-ethyl-carbinol and HI (W. a. S.).

Tert-**amyl iodide** $(CH_3)_2.CI.CH_2.CH_3$. (129°). S.G. $\frac{0}{}$ 1·524; $\frac{19}{}$ 1·50. From *iso-sec*-amyl iodide and HI (Winogradoff, *A.* 191, 132); also from *tert*-amyl alcohol and HI (Wy.). By shaking with water for $1\frac{1}{2}$ hours it is almost completely converted into *tert*-amyl alcohol (Bauer, *A.* 220, 158). With MeOH at 100° it forms MeI and *tert*-amyl alcohol; MeOAc at 110° gives amylene, MeI, and HOAc.

DI-*n*-AMYL KETONE $C_{11}H_{22}O$ *i.e.* $(C_5H_{11})_2CO$. *Caprone.* [15°]. (226° cor.). S.G. $\frac{20}{}$ ·826. Prepared by distilling calcic caproate. Does not combine with $NaHSO_3$.

Reactions.—1. Conc. HNO_3 forms caproic nitro-valeric, and oxalic acids.—2. CrO_3 forms caproic and valeric acids (E. Schmidt, *B.* 5, 601; Lieben a. Janecek, *A.* 187, 134; Hercz, *A.* 186, 263).

n-**AMYL-MALONIC ACID** $C_8H_{14}O_4$ *i.e.* $(C_5H_{11})CH(CO_2H)_2$. [82°]. Formed by saponifying the product of the action of KCy upon α-bromo-heptoic ether (Hell a. Schüle, *B.* 18, 626). Split up at 140° into CO_2 and *n*-hexoic acid.

Salts.—CaA″: S. ·04 at 18°.—SrA″: S. ·09 at 16°.—BaA″: S. ·6 at 10°.—CdA″.—PbA″: S. ·008 at 20°.—Ag_2A''.

TRI-*Iso*-AMYL-MELAMINE $C_{18}H_{36}N_6$ *i.e.* $C_3H_3(C_5H_{11})_3N_6$. Formed by desulphuration of isoamyl thiocarbimide (Hofmann, *B.* 3, 264). Thick oil.—$B''H_2PtCl_6$.

Iso-**AMYL MERCAPTAN** $C_5H_{12}S$ *i.e.* $C_5H_{11}SH$. Mol. w. 104. (120° i.V.) (Beckmann); (118°) (Nasini, *G.* 1883, 302). S.G. $\frac{20}{4}$ ·8348. R_∞ 31·94 (N.). From isoamyl chloride and KHS (Balard, *A.* 52, 313) or $C_5H_{11}SO_4K$ (Krutzsch, *J. pr.* 31, 1).

AMYL MUSTARD OIL *v.* AMYL THIO-CARBIMIDE.

AMYL-NAPHTHALENES $C_{15}H_{18}$.

(α)-*Iso*-**amyl-naphthalene** $C_{10}H_7.C_5H_{11}$ [1]. Formed by heating an ethereal solution of (α)-bromo-naphthalene and isoamyl bromide with Na (Leone, *G.* 12, 209).—**Picrate**, [85°–90°]: pale yellow needles.

(β) - *Iso*-amyl - naphthalene $C_{10}H_7.C_5H_{11}$ [?]. (c. 290°). From naphthalene, isoamyl chloride, and $AlCl_3$ (Roux, *Bl.* [2] 41, 379).—*Picrate* $C_{15}H_{18}C_6H_2(NO_2)_3OH$. [105°–110°].

Amyl-naphthalene (?). (305°). From lapachic acid, HI and P (Paterno, *G.* 12, 369).—*Picrate* [141°]: orange needles.

Iso-**AMYL NITRATE** $C_5H_{11}NO_3$. Mol. w. 133. (147°). S.V. 153·59 (R. Schiff, *B.* 19, 567). From urea nitrate (10 g.), isoamyl alcohol (40 g.) and HNO_3 (30 g.) (P. W. Hofmann, *A. Ch.* [3] 23, 374). Liquid, smelling like bugs.

Iso-**AMYL NITRITE** $C_5H_{11}NO_2$. Mol. w. 117. (96°) (B.). (99°) (Guthrie, *A.* 111, 82). S.G. ·9. H.F.p. 48,140. H.F.v. 44,660 (*Th.*).

Preparation. — 1. Nitrous vapours (from As_2O_3 and HNO_3 of S.G. 1·52) are passed into isoamyl alcohol (Balard, *A. Ch.* [3] 12, 318; Hilger, *Ar. Ph.* [3] 4, 485; Williams a. Smith, *Ph.* [3] 16, 409). — 2. By distilling together KNO_2, isoamyl alcohol, and dilute H_2SO_4 (Rennard, *Russ. Zeitschr. Pharm.* 1874, 1). Yellowish liquid, smelling like nitrous ether.

AMYLNITROUS ACID, so-called. $C_5H_{10}N_2O_4$. Obtained by action of HNO_3 on di-amyl ketone (Chancel, *C. R.* 94, 399). Liquid; may be reduced to *n*-valeric acid.

Salt.—$C_5H_9KN_2O_4$: greasy-looking plates.

AMYLODEXTRIN *v.* DEXTRIN.

AMYLOID *v.* STARCH.

AMYLONITROPHOSPHOROUS ACID, so-called. $C_{10}H_{23}PNO_4$ (?). An oil, got by action of P_2O_5 on isoamyl nitrite (Guthrie, *A.* 111, 85).

AMYL OXALATE *v.* OXALIC ACID.

Iso-**AMYL OXAMIDE** $C_7H_{14}N_2O_2$ *i.e.* $NH_2.CO.CO.NHC_5H_{11}$. [181°]. From isobutyl-isoamyl glyoxaline and H_2O_2 (Radziszewsky a. Szul, *B.* 17, 1296).

Di-*iso*-amyl oxamide $C_{12}H_{24}N_2O_2$ *i.e.* $C_5H_{11}.NH.CO.CO.NHC_5H_{11}$. [129°] (Wallach a. Schulze, *B.* 13, 516). [139°] (Wurtz). Silky needles; insol. water. From isoamylamine and ethyl oxalate.

AMYL-OXANTHRANOL *v.* OXANTHRANOL.

AMYL OXIDE $C_{10}H_{22}O$. *Amyl ether.* M. w. 158.

Iso-**amyl oxide** $(C_5H_{11})_2O$. (173°). S.G. $\frac{15}{15}$ ·7807; $\frac{23}{23}$ ·7741. M.M. 11·168 at 15·6° (Perkin, *C. J.* 45, 474). From potassium isoamylate and amyl iodide.

Iso-sec-**amyl oxide** $(Pr.CMeH)_2O$. (163°). From Pr.CMeHI and Ag_2O (Wurtz, *A.* 129, 366).

Iso-**AMYL-PHENOL** $C_{11}H_{16}O$ *i.e.* $C_5H_{11}.C_6H_4.OH$ [1:4]. [93°]. (250°). Formed by heating phenol with isoamyl alcohol and $ZnCl_2$ at 180° (Liebmann, *B.* 15, 151) or by the action of nitrous acid upon amido-phenyl-isopentane (Calm, *B.* 15, 1646). Long needles; sl. sol. water.

Benzoyl derivative $C_{10}H_{15}OBz$. [81°]. (349° cor.). Flat needles, formed by distilling tri-isoamyl phosphate with NaOBz (Kreysler, *B.* 18, 1717).

AMYL-PHENYL- *v.* PHENYL-AMYL-.

Iso-**AMYL-PHENYL PHOSPHATE** $C_{33}H_{45}PO_4$ *i.e.* $(C_5H_{11}.C_6H_4.O)_3PO$. (above 400°). Formed by heating isoamyl-phenol with $POCl_3$ (Kreysler, *B.* 18, 1701). Thick oil; v. sol. ether, sol. alcohol.

Iso-**AMYL-PHENYL SILICATE** $C_{44}H_{60}SiO_4$ *i.e.* $(C_5H_{11}.C_6H_4.O)_4Si$. (c. 394°) at 118 mm. From isoamyl-phenol and $SiCl_4$ (Hertkorn, *B.* 18, 1692).

AMYL PHOSPHATES.

Iso-**amyl-phosphoric acid** $(C_5H_{11}O).PO(OH)_2$. From syrupy phosphoric acid and amyl alcohol at ordinary temperature (Guthrie, *C. J.* 9, 134). Deliquescent crystalline mass; v. sol. water, and alcohol, insol. ether. Salts.—K_2A''.—$(NH_4)_2A''$.—BaA″.—PbA″.—CuA″.—Ag_2A''.

Di-*iso*-amyl-phosphoric acid $(C_5H_{11}O)_2PO(OH)$. From amyl alcohol and bromide of phosphorus (Kraut, *A.* 118, 102). Salts.—CaA'_2: S. 1·6 at 18°.—AgA′.—AgHA′₂.

AMYL-PHOSPHINES *v.* PHOSPHINES (Hofmann, *B.* 6, 297).

Iso-**amyl phosphine** $C_5H_{11}PH_2$. (107°).

Di-*iso*-amyl phosphine $(C_5H_{11})_2PH$. (c. 213°).

Tri-*iso*-amyl phosphine $(C_5H_{11})_3P$. (300°).

Oxide $(C_5H_{11})_3PO$. [c. 65°].

Iso-amylo-iodide $(C_5H_{11})_4PI$.

Iso-**AMYL PHOSPHINIC ACID** $C_5H_{13}PO_3$ *i.e.* $C_5H_{11}.PO(OH)_2$. *Pentane phosphinic acid.* [160°]. From isoamyl phosphine and HNO_3 (S.G. 1·35). Pearly plates (from water).

Salt.—Ag_2A'': amorphous pp. (Hofmann, *B.* 6, 305).

AMYL PHOSPHITES.

Iso-**amyl phosphorous acid** $(C_5H_{11}O)P(OH)_2$. Formed together with di-isoamyl-phosphorous acid by shaking with water the product of the action of PCl_3 on isoamyl alcohol. Dilute Na_2CO_3 dissolves mono- but not di-, amyl phosphite (Wurtz, *A. Ch.* [3] 16, 227).

Chloride $C_5H_{11}O.PCl_2$. (173°). S.G. $\frac{0}{}$ 1·109 (Menschutkin, *A.* 139, 348).

Di-*iso*-amyl-phosphorous acid $(C_5H_{11}O)_2P(OH)$. S.G. $\frac{19}{}$ ·97.

Tri-*iso*-amyl phosphite $(C_5H_{11}O)_3P$. (236°), in hydrogen. From PCl_3 and $NaOC_5H_{11}$ (Williamson a. Railton, *C. J.* 7, 218).

AMYL-PIPERIDINE $C_{10}H_{21}N$ *i.e.* $C_5H_{10}N(C_5H_{11})$. (188°). Colourless liquid, nearly insoluble in water. Formed by digesting piperidine with amyl bromide and aqueous KOH.

Methylo-iodide. B′MeI. [195°]. Thick prisms. By moist Ag_2O it gives an alkaline hydrate which on dry-distillation yields methyl-amyl-piperidine (Schotten, *B.* 15, 421).

Iso-**AMYL-PYRROL** $C_9H_{15}N$ *i.e.* $C_5H_{11}NC_4H_4$ (c. 182°). S.G. $\frac{10}{}$ ·879. Formed by distilling isoamylamine mucate (C. A. Bell, *B.* 10, 1866).

Iso-**amyl-pyrrol carboxylic acid**, *isoamylamide* $C_5H_{11}.NC_4H_3.CO.NHC_5H_{11}$. [77°]. Prisms. Formed along with the isoamyl-pyrrol (*B.*).

Iso-**AMYL SILICATE** $C_{20}H_{44}SiO_4$ *i.e.* $Si(C_5H_{11}O)_4$. (324°). S.G. $\frac{20}{}$ ·868. V.D. 15·2 (calc. 13·0). From $SiCl_4$ and isoamyl alcohol (Ebelmen, *A.* 57, 331). Oil, very slowly decomposed by water.

AMYL SULPHATES.

Iso-**amyl sulphuric acid** $C_5H_{12}SO_4$ *i.e.* $C_5H_{11}SO_4H$ (Cahours, *A. Ch.* [2] 70, 86; Kekulé, *A.* 75, 275).

Salts. — NH_4A'.—NaA′1½aq. — KA′ ½aq.— MgA'_2 4aq. — CaA'_2 2aq. — SrA'_2 2aq. — BaA'_2 2aq: flat tables, S. 9·7 at 10° (Balbiano, *B.* 9, 1437); S.G. 1·623 at 21·2° (Clarke, *B.* 11, 1506).— ZnA'_2 2aq.—HgA'_2 2aq.—PbA'_2 aq.—MnA'_2 4aq.— NiA'_2 2aq.—CuA'_2 4aq.—AgA′.

Iso-**amyl sulphate** $(C_5H_{11})_2SO_4$. Formed by passing SO_2 into warm amyl nitrite (Chapman, *B.* 3, 920).

AMYL SULPHIDES.

Di-*iso*-amyl-sulphide $(C_5H_{11})_2S$. Mol. w. 174. (214° i.V.). S.G. $\frac{20}{4}$ ·8431. R ∞ 54·2 (Nasini, *G.* 13, 302). Amyl alcohol (131°–132°) is converted by PCl_5 into amyl chloride and this is mixed with alcoholic K_2S (from half saturation of alcoholic KOH with H_2S) and heated in closed vessels for 10 hours at 100°. Product fractionated (Beckmann, *J. pr.* [2] 17, 440). Also from potassium amyl-sulphate and K_2S (Balard, *A. Ch.* [3] 12, 303).

Di-*iso*-amyl disulphide $(C_5H_{11})_2S_2$. (250°). S.G. $\frac{18}{}$ ·918. From potassium amyl-sulphate and K_2S_2 (O. Henry, *A. Ch.* [3] 25, 246; Spring a. Legros, *B.* 15, 1938).

Iso-**AMYL SULPHITE** $(C_5H_{11}O)_2SO$. (230°–250°). From $SOCl_2$ or S_2Cl_2 and isoamyl alcohol (Carius, *A.* 106, 291; 111, 97). Oil; decomposed by water or KOHAq into amyl-sulphurous acid and amyl alcohol.

AMYL SULPHOCYANIDE $C_6H_{11}NS$ *i.e.* $C_5H_{11}S.CN$. (197°). S.G. $\frac{20}{}$ ·905. Got by distilling potassium amyl-sulphate with potassium sulphocyanide (Henry, *A. Ch.* [3] 25, 248; Medlock, *A.* 69, 214).

Di-*iso*-AMYL SULPHONE $(C_5H_{11})_2SO_2$. [31°]. (295°). Di-iso-amyl sulphoxide (5 pts.) is heated with water (20 pts.) till it melts, a solution of $KMnO_4$ (3 pts.) in hot water (30 pts.) is added with constant agitation. The sulphone is extracted with ether. The yield is that indicated by theory (Beckmann, *J. pr.* [2] 17, 441).

Properties.—Long needles, grouped in tufts. Sl. sol. hot water; sol. alcohol, ether, benzene, $CHCl_3$ and CS_2. Soluble in H_2SO_4, HNO_3 and acetic acid, but precipitated by water from these solutions. Not reduced by Zn and H_2SO_4, by sodium-amalgam or by HI.

AMYL-SULPHONIC ACID *v.* PENTANE SULPHONIC ACID.

DI-*iso*-AMYL-SULPHOXIDE $(C_5H_{11})_2SO$. [37°]. From di-amyl sulphide (1 pt.) and fuming HNO_3 (2 pts.). Crystallised from ether (Saytzeff, *A.* 139, 354; Beckmann, *J. pr.* [2] 17, 441). Flexible fatty-looking crystals. Chlorine acts on it in presence of water forming pentane sulphonic acid, chloro-pentane sulphonic acid, di-isoamyl sulphone, valeric acid, chloro-valeric acid, tri- and tetra-chloro-pentanes, &c. (Spring a. Winssinger, *Bl.* [2] 41, 307).

AMYL - SULPHURIC ACID *v.* AMYL SULPHATE.

Iso-**AMYL TELLURIDE** $Te(C_5H_{11})_2$. (c. 198°). Got, in impure state, by distilling calcium amyl sulphate with TeK_2 (Wöhler a. Dean, *A.* 97, 1).

Iso - **AMYL - DI - THIO - CARBAMIC ACID** $C_6H_{13}NS_2$ *i.e.* $C_5H_{11}NH.CS.SH$. *Isoamylamine salt* $C_5H_{11}NH_2HA'$. From isoamylamine and CS_2 in ethereal solution (Hofmann, *J.* 1859, 379). Laminæ.

AMYL THIOCARBIMIDES $C_6H_{11}NS$ *i.e.* $C_5H_{11}N.CS$. *Amyl mustard oils.* Mol. w. 129.

Iso-amyl-thio-carbimide (183°). S.G. $\frac{17}{}$ ·942. Obtained by boiling the preceding compound with aqueous $HgCl_2$ (Hofmann, *B.* 1, 173; Buff, *B.* 1, 206).

Tert-amyl thio-carbimide $EtCMe_2N.CS$. (166°). From $EtCMe_2NH_2$ by successive treatment with CS_2 and $HgCl_2$ (Rudneff, *Bl.* [2] 33, 300).

AMYL THIO-PHOSPHATES.

Iso-**amyl thio-phosphate** $(C_5H_{11})H_2PSO_3$. From isoamyl alcohol and $PSCl_3$ (Chevrier, *Z.* 1869, 413).

Tri-*iso*-amyl thiophosphate $(C_5H_{11})_3PSO_3$. S.G. $\frac{12}{}$ ·85. From $C_5H_{11}ONa$ and $PSCl_3$ (C.). Oil.

Di-*iso*-amyl di-thio-phosphate $(C_5H_{11})_2HPS_2O_2$. Salt.—PbA'_2 [70°].

Tri-*iso*-amyl-tetra-thio-phosphate $(C_5H_{11})_3PS_4$. Formed, together with the preceding, when P_2S_5 acts on isoamyl alcohol (Kowalewsky, *A.* 119, 310).

Iso-**AMYL THIOSULPHATE.** The salt $Na(C_5H_{11})S_2O_3 2aq$ is formed by acting with isoamyl iodide on sodium thiosulphate. It crystallises in laminæ (Spring a. Legros, *B.* 15, 1938).

Iso-**AMYL THIO-UREA** $C_6H_{14}N_2S$ *i.e.* $C_5H_{11}NH.CS.NH_2$. Monoclinic crystals (Arzruni, *P.* 152, 284).

AMYL-TOLUENE $C_{12}H_{18}$ *i.e.* $CH_3.C_6H_4.C_5H_{11}$. *Methyl-amyl-benzene*

o-*Iso*-amyl-toluene (?). (204°). S.G. $\frac{0}{}$ ·895. From toluene, isoamyl chloride, and zinc dust (Pabst, *B.* 9, 503).

m-*Iso*-amyl-toluene. (208°). S.G. $\frac{22}{}$ ·868. From toluene, isoamyl chloride, and $AlCl_3$ (Essner a. Gossin, *Bl.* [2] 42, 213). $KMnO_4$ gives isophthalic acid.

p-*Iso*-amyl-toluene. (213°). S.G. $\frac{0}{}$ ·864. From *p*-bromo-toluene, isoamyl bromide, and Na (Bigot a. Fittig, *A.* 141, 160). CrO_3 produces terephthalic acid.

AMYLUM *v.* STARCH.

AMYL-UREA $C_6H_{14}N_2O$ *i.e.* $C_5H_{11}NH.CO.NH_2$.

Iso-amyl-urea [91°]. From amyl cyanate and hot alcoholic NH_3 (Custer, *B.* 12, 1330; *cf.* Wurtz, *C. R.* 32, 417; *Bl.* [2] 7, 141). Crystals; sl. sol. water.

Iso-Hexoyl-derivative $C_5H_{11}NH.CO.NH.CO.C_5H_{11}$. [94°]. From the amide of isohexoic acid, $Pr.CH_2.CH_2.CO_2H$, by means of Br and NaOH (Hofmann, *B.* 15, 758).

Tert-amyl-urea. [151°]. S. 1·26 at 27°. From tert-amyl cyanate and NH_3 (Wurtz, *A.* 139, 328).

n-Hexoyl derivative. [97°]. Formed by action of potash on a mixture of *n*-hexamide and bromine (H.). Plates; sol. alcohol, and ether, insol. water.

Di-*iso*-amyl-urea $C_5H_{11}NH.CO.NHC_5H_{11}$. [39°]. (270°). Formed by boiling isoamyl cyanate with isoamylamine and alcohol (C.). Needles; insol. water, sol. alcohol and ether.

Di-*tert*-amyl-urea. Formed by action of KOH upon tert-amyl cyanate (W.). Needles; may be sublimed.

Tri-*iso*-amyl-urea $(C_5H_{11})_2N.CO.NH.C_5H_{11}$. (260°). From isoamyl cyanate and di-isoamylamine (C.). Liquid.

Tetra-*iso*-amyl-urea $(C_5H_{11})_2N.CO.N(C_5H_{11})_2$. (241°). Obtained by the action of $Cl.CO_2Et$ upon a mixture of di- and tri- isoamylamine (C.).

AMYL URETHANE *v.* AMYL-CARBAMIC ETHER.

AMYL-VALERONE *v.* BUTYL ENNYL KETONE.

Iso-**AMYL-XYLENE** $C_{13}H_{20}$ *i.e.* $C_6H_3Me_2.C_5H_{11}$. *Di-methyl-isoamyl-benzene.* (233°). S.G. $\frac{0}{}$ ·895. From bromo-xylene, isoamyl bromide and Na (Fittig a. Bigot, *A.* 141, 168).

AMYRIN. A crystalline resin, difficultly soluble in alcohol, contained in some specimens of elemi, and in arbol-a-brea resin (Buri, *Neues Repert. für Pharm.* 25, 193; Hesse, *A.* 192, 179). According to Hesse its formula is $C_{47}H_{76}(OH)_2$ and its acetyl derivative is $C_{47}H_{76}(OAc)_2$. Bromine forms a complicated bromo-derivative.

ANACARDIC ACID $C_{22}H_{32}O_3$. [26°]. Occurs in the fruit of *Anacardium occidentale* (Staedeler, *A.* 63, 137). Crystals; insol. water, v. sol. alcohol and ether. Salts.—CaA″aq.—BaA″.—PbA″.—HA″PbOAc.—A″FeOH aq. —AgHA″.

ANALYSIS. To analyse a thing means to resolve it (ἀναλύειν) into its components. This term, however, has a very wide meaning, which stretches far beyond the outermost limits of our resources of even *virtual* analysis. So well is this understood by all that even when we speak of a complete analysis we refer only to as complete a solution as the science affords of one or other of three special problems. One of these is the actual or virtual resolution of the body into its component chemical species or perhaps genera; another, the determination of its elements; the third, the determination of what, in the sense of some imagined general mode of decomposition, are its primary radicles. This (the last named) problem has received a partial solution in the sense that we have ready-made methods for the determination of the acids and bases that may be contained in a solution of salts of a certain low order of complexity. These methods include only a minority of the non-metallic salt radicles, but they include all the better-known elements as such; and as we have general methods for converting any kind of substance into salts of low order of complexity, these latter methods, conjointly with the former, constitute a complete solution of the problem of *ultimate analysis*. In regard to the first problem, our powers are very limited. That we have methods for the proximate analysis of certain classes of substances need not be specially affirmed; without these, vegetable and animal chemistry could have no existence—but a general exposition of their principles would resolve itself into the retailing of commonplaces. We prefer to give a brief summary of what we have of means and ways for seeing whether a substance presumed to be pure really is one substance or is a mixture. In a sense there is only one method: we subject the substance to some physical or chemical process of fractionation, which, while sure not to produce transmutations, gives the several proximate components a chance of parting from one another; and we then compare the several products with one another and with the original substance. The form which the method assumes depends largely on the state of aggregation of the substance under operation.

I. Gases. The oneness of a gas can in general be proved by (*a*) *fractional diffusion* through a septum of gypsum or graphite; if the gas is a mixture of, say, two species, the lighter one diffuses out faster than the other; with mixtures of gases of the same specific gravity, the method, of course, breaks down: (*b*) *partial absorption*. This method is discussed fully under 'gas-analysis' (*q. v.*).

II. Solids. These may be susceptible of fractionation by (*a*) *partial fusion*; (*b*) *partial solution* in suitable solvents; (*c*) *partial freezing of the liquefied body*; (*d*) *partial crystallisation* out of solutions; (*e*) *partial volatilisation.* (See III.) For the comparison of the several fractions, the determination of the fusing points comes in as a handy, and in general sensitive, test.

III. Liquids. For these the methods given under (*b*) and (*c*) for solids may be available. In the case of distillable liquids we generally resort to fractional distillation, taking care to observe the temperature of the (saturated) vapour, during the progress of the operation. A mixture may have a constant boiling-point, and may besides remain undecomposed on distillation; as a rule, however, it is not so. The volatility of each component depends chiefly on the value for it of the product mp, where m is the molecular weight (or vapour density), and p the vapour-pressure at the prevailing temperature of ebullition. For two components, the respective products m_1p_1 and m_2p_2 have in general different values. Hence it is not necessarily the lowest boiling component which comes over first; because a large m may make up for a small p. As a mere test for purity, the determination (at a series of suitable temperatures) of the vapour-pressure by the statical method goes considerably further than the determination of the boiling-point curve. In a pure substance, the pressure, p, at $t°$ is a function of t only; in a mixture of (say) two liquids, p depends (in a given trial) on the volume of vapour produced, because the ratio of the weight of the vapour to that of the unvolatilised residue changes with this volume. If this ratio is very small, we have an approximation to the vapour-pressure of the more volatile component; if the ratio is large, the pressure approaches the value characteristic of the mixture as such. Any of the many mixtures of constant boiling-point, when subjected to this test, at a suitable temperature, is sure to reveal its complexity. Unfortunately the operations involved are somewhat troublesome, and the results are liable to be largely vitiated by the presence of absorbed air in the sample.

The second and third of our three general problems, qualitatively considered, form the body of what is customarily being taught as

Qualitative Analysis.

The resources of qualitative analysis—apart from mere methods of identification of named species, which we leave on one side—may be arranged under three heads:—

I. Flame Tests. A set of methods for the detection of elements as such, which, being all founded upon ultimate or penultimate dissociations at high temperatures, are in a high degree independent of the constitution of the substance operated upon. Another specific feature in these tests is that they are easy and rapid of execution, and demand only very small quantities of substance.

II. A set of what we will call methods of chemical disintegration (each general in reference to a large class of bodies), by means of which compounds of high chemical complexity can be, so to say, opened up, and their elements

brought within the range of our routine methods of salt analysis (*v. infra*). These methods might, each, be indexed, by reference to a certain element, generally of high valency; as a rule it is a non-metallic element, and in the analyst's sense, *sui generis*, *i.e.* not susceptible of detection as one of a group.

III. **The systematic methods for the radical analysis of a solution of salts** which were referred to in the introduction. In addition to these analytical methods, the analyst naturally discounts all that may help him towards the solution of his problem. Our three classes of methods alone, it is true, if judiciously employed, would enable one in general to perform an exhaustive ultimate analysis; but a purely ultimate analysis, in the majority of cases, is not what we want. The ideal which we aim at in all analyses made for practical purposes is (as good an apology as is attainable for) a proximate analysis; a recipe, so to say, for composing the substance from things of known constitution. Hence, if the substance presents the aspect of a mixture—mechanical or physical—we naturally begin by trying to effect a separation of the several things from one another: by mere picking out, or elutriation, in the case of an obvious mixture; by distillation in the case of a solution in a volatile solvent. We will assume, however, that this division of the given substance into two or more substances has been effected (if called for, and possible), and that the substance to be analysed is a solid (which virtually includes the case of a liquid); gases demand special methods, which lie beyond our programme. In this, as in any analogous case, we naturally begin by a close observation of at least the general properties of the body; it may be expedient to supplement this observation by the exact determination of certain physical properties, such as hardness, specific gravity, crystalline form, optical constants, &c., &c. Everything here depends on the nature of the case, and—of the operator. A mineralogist, for instance, by such determinations, may be able virtually to analyse a mineral; but everybody cannot do this. After the more purely observational stage, it is expedient to study the behaviour, at a graduated succession of high temperatures, of (*a*) the substance itself, (*b*) the substance and atmospheric oxygen, (*c*) the substance plus added reagents. We therefore begin by heating a few centigrams of substance in a sublimation tube over a Bunsen lamp—first gently, then more and more strongly —on the chance of obtaining a readily recognisable sublimate, gas or vapour, or residue. Of the identifiable residues, charcoal is the most important, because its formation proves the presence of *organic* matter in the sample, although all organic matter does not yield charcoal. If 372 substance presents a metallic, or semi-
llic, aspect, it is expedient to roast a frag-
in a draught-tube, on the chance of
a sublimate of mercury, oxide of
white arsenic, iodine, &c., or an
sulphurous acid, &c. If the sub-
s partially volatile or partially
we prepare a supply of the fire-proof
west sufficient temperature), and,
the first as we would a fire-proof
bject it to a selection of

I. Flame Tests.

By "flame-tests" we mean dry-way tests, in which the substance, or substance plus reagents, is heated directly in the flame. These tests were introduced by Gahn, and subsequently extended and brought to high perfection chiefly by Berzelius and Plattner. In accordance with the modes of operating which these authorities found it convenient to adopt, a blowpipe flame used to be universally employed as a heating medium. But Bunsen, some twenty years ago, showed that most blowpipe tests can be done more easily and conveniently in the flame of the gas lamp which bears his name, and that this flame can also be employed for certain new tests introduced by him, which tests could not be conveniently done with the blowpipe. Many chemists prefer the Bunsenian *modus operandi*, but the blowpipe has not by any means become obsolete; it will continue to be used, because it offers certain specific advantages of its own. For the purposes of this article it will be sufficient to give the following enumeration of the more important of the characteristic flame-test operations:

(1.) A few mgms. of the substance are placed on an asbestos-stick, and exposed to the several regions of a Bunsen-flame, proceeding from lower to higher temperatures, to determine degrees of fusibility and volatility.

(2.) A few mgms., fixed to one end of a hair-fine platinum wire, are exposed first to colder, and then to the hottest, part of the flame-mantle of a Bunsen, in order to see whether the flame is thereby coloured. If a colour is produced, it is analysed optically (by means of a spectroscope), with the view of thus effecting a chemical analysis of the glowing vapour. Of elements identifiable by their spectra (or flame colours), the following may be named:—Tl, In, Rb, Cs, K, Na, Li, Ba, Sr, Ca in most of the ordinary states of combination, Cu as haloid salts, B as boric acid or fluoride, P as free phosphoric acid or PH_3.

Spectrum analysis, as everybody knows, was invented by Bunsen and Kirchoff. Some years ago Bunsen brought it into a new form, in which a spark current, produced by means of an induction-coil, is used for the volatilisation of the substance; at the very high temperatures thus produced, a great many elements, besides those named, become identifiable by their spectra.

Flame Tests with Reagents.—Of these *sodium carbonate* is most extensively employed; either platinum wire or charcoal being used as a support.

On platinum; (1) as a mere flux, it identifies SiO_2, given as such or as highly acid silicate; (2) in conjunction with oxygen used as air, or introduced as nitre—it detects Cr and Mn with certainty, converting the former into (yellow) chromate, the latter into (green) manganate.

When used on charcoal; in the reducing flame, it may bring to light, (1) S, Se, Te. Any non-volatile form of these yields a fused mass, containing Na_2S &c., recognisable by the black stain (Ag_2S &c.) which it produces when placed on a silver coin, and moistened with a drop of

water.—(2) *One or more of the following metals*; As, Hg, Zn, Cd, Pb, Bi, Sn, Cu, Ag, Au, Fe, Ni, Co, Pt. The oxides and many of the salts of these metals when subjected to the operation under discussion, are reduced to the elementary state. The metal thus liberated may assume the form of a visible fused bead, or remain concealed in the form of fused scales or an unfused powder or sponge; these, however, can in all cases be isolated and brought to light by elutriation with water in an agate mortar. Part of the metal, in general, volatilises, and in passing through the flame becomes oxide. If the reduction is effected in the blowpipe flame on a block of charcoal (old style), part of the oxide in general settles down on the charcoal as a ring, and by its colour may aid in identifying the metal. When operated upon as described, compounds of As yield only vapour of oxide, which in most cases is lost altogether. Hg; vapour of metal, which is also lost. Zn, Cd; little or no metal, but abundant oxide rings; (ZnO is white, CdO brown). Pb, Bi; easily fusible metal, and tangible quantities of yellow oxide. Sn; easily fusible metal, and little (white) oxide. Cu; not easily—Ag; more easily —Au; not easily—fusible metal or scales, and no oxide. Fe, Ni, Co; unfused powdery, or spongy, metal, which follows the magnet. No oxide. Pt; like Fe, but the metal is not magnetic and is unacted on by HNO_3Aq.

In Bunsen's mode of operating—which consists in heating the mixture of substance and soda on a slender stick of charcoal in the reducing part of the 'zone of fusion,' the oxide is lost, but all the respective metals fall within the range of

Bunsen's Film Tests.—When the air-holes of the Bunsen are partially closed, a luminous tip forms somewhere near the apex of the flame. Many oxides suffer reduction when held in the centre of this tip on an asbestos stick; and the reduced elementary substance can be collected on a Berlin basin (filled with water to keep it cold), held over the sample across the flame. The elements thus appear as films resembling the stains of As and Sb produced in Marsh's test. The following elements chiefly yield films: As, Sb, Te, Se; hardly attacked by nitric acid of 20 p.c. Bi, Hg, Tl; very slowly dissolved by nitric acid of 20 p.c. Pb, Cd, Zn, In; instantly dissolved by nitric acid of 20 p.c. By a very obvious modification of the process, oxide films can be produced in lieu of metallic ones; but we cannot go any further into this matter.

Borax is always used as a bead fused to the end of a platinum wire. Such a bead dissolves most metallic oxides at a moderately high temperature, forming glasses, the colours of many of which are characteristic of the metal. Often one metal gives two colours according to whether the fusion is effected in the oxidising or in the reducing flame; this affords additional means of discrimination.

Microcosmic salt (or rather the fused $Na_2O.P_2O_5$ produced by its decomposition by heat) acts on metallic oxides pretty much as borax does; but its specific function is the detection of *silica*. If a splinter of a silicate is heated in a fused meta-phosphate bead, the bases dissolve out, the silica remains in the characteristic form of an unfused 'skeleton' of the splinter.

Whatever the flame-tests may have brought out by way of positive results, their negative results count for very little.

II. Methods of Chemical Disintegration.

Substances may be divided into two classes, as regards the operations required to bring them within the range of our systematic methods of salt-analysis. (1) Such as are simple salts (we mean salts which can be analysed by our routine methods), or can be made into solutions of such by the application of the ordinary mineral solvents, such as water, dilute mineral acids (*qua* acids), nitric acid or aqua regia (*qua* oxidants). This class comprises many minerals, and ordinary chemical bodies, but unfortunately (and naturally) we have no general test for the recognition of these bodies as a class. (2) Such as demand special methods of disintegration. Of the more commonly occurring chemical genera, the following may be named as falling within this class:—(*a*) *Fluorides*; these although perhaps of the simplest constitution, demand special methods because hydrofluoric acid and all acid fluoride-solutions attack glass and porcelain. (*b*) Most *silicates*: *silico-fluorides*. (*c*) *Cyanides*, especially *metallocyanides*. (*d*) *Salts of certain complex organic acids* (not cyanides); in the sense that they exhibit abnormal metal-reactions. (*e*) *Organic compounds* generally; in the sense of ultimate analysis generally. (*f*) *An-orthophosphates*. (*g*) Certain classes of *sulphur compounds*.

This list does not pretend to be complete, but it includes most bodies which the practical analyst is likely to come across. For the second class of substances as a class, we of course have not a general test any more than we have for the first, but we have general tests for the several genera, in this sense at least that we have general methods for the detection of their characteristic elements.

The following section is compiled partly with the view of supplying the necessary information in this direction.

General methods for the detection of certain elements (mostly non-metals) and for the ultimate analysis of their compounds.

Silicon is always isolated in its highly characteristic form of *silica*, SiO_2, which is easily identified by the blowpipe tests given above, and by its convertibility into volatile SiF_4 by the action of HF. *Silicon and metallic silicides*, when fused with caustic alkali, yield alkaline silicates (*q. v.*). *Alkaline silicates* (even if so acid as $R_2O.4SiO_2$) dissolve in water, forming alkaline solutions. *Mineral silicates, Slags, Glasses, &c.* fall within two classes according to whether they are, or are not, decomposable by hydrochloric acid. Those of the first class are finely powdered and digested in conc. hot HClAq until disintegrated, evaporated to *complete* dryness (to convert the colloidal part of the silica into the insoluble form), drenched with HClAq, allowed to stand (to re-chlorinate the Al_2O_3 and Fe_2O

produced), treated with water, and filtered. The silica remains on the filter; the solution contains the metals as chlorides. Of those of the second class, some are disintegrable by hot semi-conc. H_2SO_4Aq (ex. the clays). The general method is to fuse the finely powdered silicate with $KNaCO_3$ until all is dissolved, and to analyse the fused residue as a silicate of the first class. Alkalis must be tested for in another portion of the silicate, after evaporation with NH_4FAq, whereby Si is removed as SiF_4 and the bases remain as fluorides easily convertible into sulphates by H_2SO_4Aq (comp. Fluorine).

Aluminium.—Only the forms of Al_2O_3 insoluble in acids need be considered here; these if *finely enough divided*, all dissolve at a red-heat in fused KOH, becoming aluminates soluble in water.

Chromium.—All non-volatile compounds, when fused (in silver) with KOH and KNO_3, yield alkaline *chromate*, recognisable by its yellow colour and the *very* intensely yellow colour of its aqueous solution. This operation constitutes a general method of disintegration for the forms of Cr_2O_3 and chromites insoluble in acids; it goes a certain way even with *chrome iron ore*, but the complete disintegration of this mineral demands special methods.

Titanium.—TiO_2 stands between SiO_2 and Al_2O_3. Unlike the former it is not volatilised by evaporation with HFAq. Titanates are decomposed by fusion with $KHSO_4$; the cold aqueous extract after fusion includes the TiO_2 which is precipitated on boiling, as such.

Tin.—The forms of SnO_2 (including tinstone) which are insoluble in acids yield Sn when fused on charcoal with $NaHCO_3$ and KCN. They may be disintegrated (1) by fusion with KOH; the SnO_2 becomes stannate soluble in water: (2) by fusion with six pts. S and six pts. Na_2CO_3; the aqueous extract after fusion contains the Sn (also any As and W that may be present) as *thiosalt*, and consequently falls in with a certain stage of the routine method of metal-analysis (*v. infra*).

Carbon in any state of combination is convertible into CO_2, which is readily identified. It is distinguished from HCl and SO_2 by its scanty solubility in water, and inertness towards oxidising agents; from N, H, &c. by its abundant solubility in solutions of basic hydrates; with CaO_2H_2Aq and BaO_2H_2Aq it gives a characteristic white pp. of carbonate. *Carbonates* (almost without exception) are decomposed by mineral acids with evolution of CO_2. *Elementary carbon* (in all forms) burns in oxygen to CO_2.

Combustible Carbon Compounds.—The methods of organic analysis (*q. v.*) are easily translated into general methods for the detection of combustible carbon as CO_2. It is *necessary* to purify the CuO or $PbCrO_4$ immediately before use by heating it to redness in air until it ceases to give off CO_2.

• All non-volatile carbon compounds can be burnt by heating them with conc. H_2SO_4Aq and CrO_3. Many volatile organic bodies unite readily with conc. H_2SO_4Aq to form non-volatile compounds, and thus fall within the range of the method which obviously suggests itself for the detection of *combustible carbon beside carbonate.*

Analysis of Carbon Compounds.—I. *Organic acids proper* (COOH compounds) need here be considered only in regard to the extent to which they interfere with the routine methods for the detection of the metals in a solution of salts. Some (including formic, acetic, succinic, and *many* others) interfere only in this sense that, in their presence, the precipitate obtained by H_2S in the presence of free acid, may include Zn, Co, Ni, and perhaps other metals of the iron group. This difficulty is easily overcome. A large class of non-volatile acids, including the ordinary fruit acids, prevent the precipitation of Fe_2O_3, Al_2O_3, Cr_2O_3, CuO, and other metallic oxides by alkalis, and that of Al and Cr even by sulphide of ammonium. In all difficult or doubtful cases, it is best to destroy the organic part of the salt, which can be done in two ways:—(1) *By incineration*: which, of course, had better be postponed until after the elimination of the copper and arsenic groups by sulphuretted hydrogen; if this has been effected, Zn, of all the metals left, is the only one which may be lost by volatilisation.—(2) By *treatment* (of the dry salts) *with oil of vitriol*. The ultimate product contains the metals in the form of sulphates.

II. *Cyanides. a.* Hydrocyanic acid; easily recognised by its volatility and specific smell and reactions; regarding the latter, see *b*. *b.* The simple cyanides of the more positive metals (K to Ca inclusive). These are all soluble in water. The solutions are alkaline, and give off HCN with acids. $AgNO_3Aq$ in excess precipitates AgNC, insoluble in dilute HNO_3Aq. When mixed with (1) excess of alkali, (2) ferroso-ferric salt, (3) excess of HClAq, they yield a blue precipitate (or green suspension) of Prussian blue. *c.* Cyanide of mercury, $Hg(NC)_2$. Soluble in water. Exhibits anomalous reactions both as a mercuric salt and as a cyanide. But is decomposed by H_2S into a pp. of HgS and a solution of HCN. *d.* Heavy metallic cyanides, and metallocyanides. Some give off part of their cyanogen as HNC, when distilled with dilute HClAq or H_2SO_4Aq. Many (*e.g.* prussiates) recognisable by specific tests. Solutions of metallocyanides mostly give pps. with $AgNO_3Aq$, insoluble in dilute HNO_3Aq, in which the characteristic metals of the radicles can be detected (*v.* Halogens).

A general method for the detection of the metals in cyanides, cyanates, and thiocyanates, is to heat the dry substance with conc. H_2SO_4Aq until completely decomposed. The cyanogen becomes ammonia-salt, and CO; the metals remain as sulphates. About the detection of non-metallic elements in carbon compounds, see sect. on S, P, &c.

Boron occurs chiefly in the form of borate. The presence of boric acid does not interfere with the routine methods of metal analysis.

Phosphorus is always isolated and identified as orthophosphate. I. *Orthophosphates*, as far as not soluble in water, are mostly soluble in HClAq. To search for phosphoric acid, we supersaturate the solution strongly with ammonia, and (after filtration, if necessary) add magnesia mixture (NH_4Cl and $MgCl_2$ in NH_3Aq), crystalline $PO_4MgNH_4.6H_2O$ gradually forms, insoluble in dilute NH_3Aq. A pp. formed by

NH_3Aq generally contains part, sometimes the whole, of the phosphoric acid. To detect the latter we dissolve the pp. in HNO_3Aq, add excess of a nitric solution of molybdate of ammonia, and allow to stand at 40°C. All the phosphoric acid comes down gradually as a yellow powdery pp. of phospho-molybdate of ammonia, insoluble in excess of reagent, but soluble in excess of acid phosphate; soluble in ammonia. Both reactions are very delicate, and, in the absence of arsenic acid (which in the circumstances behaves like phosphoric), highly characteristic. Phosphates in any other state of combination can be brought into the orthophosphate form by suitable operations. II. *Meta- and pyrophosphates* (which besides being different in their own reactions from orthophosphates, exhibit anomalous metal-reactions); by long-continued boiling with mineral acids, or (what is better) fusion with carbonate of alkali. III. *Elementary phosphorus*, and all oxidisable phosphorus compounds; by treatment with HNO_3Aq of the proper strength at the proper temperature. Many organic phosphorus compounds, it is true, cannot be thus completely oxidised, but in their case, we need only neutralise the nitric liquor produced with potash, evaporate to dryness, and fuse the residue with KOH, to convert all the phosphorus into orthophosphate.

Sulphur.—Analytically speaking, sulphuric acid is to sulphur what orthophosphoric acid is to phosphorus. I. *Sulphates*, in an aqueous or HCl solution, are separated out completely by $BaCl_2Aq$, as white, powdery, $BaSO_4$, insoluble in aqueous mineral acids, and thus distinguished from all the baryta-pps., except the selenate and fluosilicate. $BaSeO_4$ is decomposed by boiling HClAq with formation of Cl and SeO_2, while $BaSO_4$ is not so decomposed. The fluosilicate yields *no sulphide* on fusion with Na_2CO_3 on charcoal; and dissolved fluosilicates give no pp. with $SrCl_2Aq$, while sulphates yield a pp. of $SrSO_4$, slightly soluble in dilute acids. II. *Acid-insoluble sulphates* are disintegrated by fusion with alkaline carbonate, and treatment with water; a solution of alkaline sulphate, and a residue of the respective carbonate, oxide, or metal, are obtained. III. *Metallic sulphides.*—Many are decomposed by HClAq with evolution of H_2S. IV. *The salts of the lower sulphur acids*, when heated (in solution) with alkaline permanganate are completely oxidised with ppn. of manganite, $MnO_2.R_2O$. The excess of oxidant used is brought into the same form by addition of a few drops of alcohol. The filtrate contains all the sulphur as sulphate. Only dithionic acid does not yield readily to this process of oxidation. All the sulphur compounds III. and IV., including dithionates, and *many organic sulphur compounds*, are oxidised completely by hot, sufficiently conc. HNO_3Aq. Volatile compounds (such as CS_2) must be manipulated in a sealed glass tube. From some organic bodies only sulphonic acids are produced; but these, when fused with KOH and KNO_3 all yield up their sulphur as sulphate.

All oxidisable sulphur compounds are completely oxidised to sulphates by the action of basic reagents (like Na_2CO_3, CaO, &c.), and KNO_3, or even oxygen-gas, at a red heat. All non-volatile sulphur compounds yield alkaline sulphide when fused with Na_2CO_3 on charcoal in the reducing flame (*v.* FLAME TESTS).

Selenion and Tellurium are closely allied to sulphur, but must be passed over.

Nitrogen, in all states of combination, is susceptible of elimination as nitrogen gas, recognisable by the methods of gas-analysis. Another less general, yet widely applicable and more convenient, method is based upon the conversion of the element into ammonia.

I. *Ammonia*; recognisable by its smell, its great solubility in water, its ready union with HCl to form solid NH_4Cl, &c. The least traces of NH_3, or NH_4 salt in water, are detected by Nessler's reagent (a solution of HgI_2 and KI in KOHAq); iodide of mercurammonium separates from moderately dilute solutions, as a brown pp., and even in the most dilute solutions is visible as a brown or yellow colour. II. *Ammonia salts*; many amides (including all acid-amides) when distilled with caustic alkali, yield NH_3 which passes into the distillate. III. *Nitrates and nitrites* in alkaline solutions are reduced by *nascent hydrogen* (KOHAq and Al) to NH_3. IV. *Metallic nitrides*, and all organic nitrogen compounds not containing their nitrogen in the form of oxygenated radicles or in the diazo-form, when burnt with soda lime yield their N as NH_3.

Fluorine. Most metallic fluorides, when treated (as powders) with conc. H_2SO_4Aq in a platinum crucible at a gentle heat, give off HF, recognisable by its etching glass and even rock-crystal. For the purpose of metal-detection, the mass must be evaporated until a tangible quantity of sulphuric acid has gone off as a heavy vapour. The bases remain as sulphates.

Mixtures of *fluorides and silicates*, when heated with conc. H_2SO_4Aq give off SiF_4, decomposed by water into H_2SiF_6Aq and a gelatinous pp. of SiO_2, which, however, may be invisible. To detect the fluorine, add excess of ammonia to bring down all the silicon as silica (which filter off), and evaporate the filtrate in platinum on a water-bath nearly to dryness. Residue is fluoride of ammonium.

Fluosilicates. Those of the most basylous metals when heated dry break up into SiF_4 and a residue of fluoride. Fluosilicates generally behave to boiling alkali solutions as if the silicon were a basylous metal.

The Halogens (Cl, Br, I). I. *The elementary substances* are recognised by their very characteristic properties. When treated with zinc and water, they all dissolve as haloid salts of zinc ($ZnCl_2$, &c.). II. *Haloid salts*; mostly dissolve in water or in HNO_3Aq. Even from the latter solution the halogen is completely ppd. as haloid salt of silver, insoluble in dilute mineral acid. III. *The oxygen acids of the halogens.* (Periodic acid ignored.) Of these only bromic and iodic give silver pps. insoluble (or soluble with difficulty) in cold, dilute, HNO_3Aq. All the rest form soluble silver salts. Their alkali and alkaline-earth salts when heated dry give off oxygen and become haloid salts. With the only exception of *perchloric acid* they are all reduced by SO_2Aq to halogen-hydride (*e.g.* $HClO_3$ to HCl). Hence an obvious IV. *Relatively general method for the detection of halogen in a solution of salts.* The solution

(which we will assume to be neutral or acid) is mixed with excess of SO_4Aq and $AgNO_3Aq$, the pp. is allowed to form, and then treated with HNO_3Aq, to remove foreign salts (including Ag_2SO_4 which is not very readily dissolved). The pp. contains all the halogen of the solution, (except that of the perchloric acid); but it may besides contain—if it does not consist of—cyanide, thio-cyanate, and metallo-cyanates, of silver, (not to mention the sulphide which is easily kept out). An analysis can be effected by calcining the dry pp. with chemically pure soda-lime, preferably in a current of moist hydrogen. The nitrogen of the cyanogen radicles goes off as ammonia, which is easily identified. The residual product contains the metals of the metallo-cyanates as oxides, the silver as metal, the sulphur of the sulphocyanogen as alkaline sulphide, and the halogens as alkaline haloids.

V. *Organic halogen compounds.* All these, when burnt with quick-lime in a combustion tube, yield up their halogen as haloid salt of calcium, extractable by cold, dilute, HNO_3Aq.

III. Methods for the Systematic Examination of a Solution of Salts for its Metals

can be given only on the basis of restrictive assumptions. We assume, in the outset at least, that the solution is so constituted that it might have been prepared by dissolving a set of basic or acid metallic oxides in aqueous mineral acid or alkali, and that certain rare oxides and certain rare combinations of things are absent. Some of the cases lying beyond this programme are dealt with in appended notes to which reference is made in the context. For the sake of generality, however, we assume that all the more ordinary metallic radicles may be present. It evidently would not do to search for them individually and seriatim; the only course one could reasonably think of is to begin by splitting up the given complex group of metals into a number of groups, so that each of these shall contain the whole of, and nothing but, certain metals, A, B, C, . . .; to then apply the same principle to the groups; and then to the groups of the second order; and so on until one arrives at last at either the individual metals, or at groups of such smallness that the side-by-side recognition of their members offers no difficulty. This, at any rate, is the course which is adopted by every chemist. The table on p. 221 in its first vertical column names the generic reagents which are customarily used for the formation of primary groups, and shows how these act on solutions of the groups of oxides named in the successive column headings. For the *separation* of the groups from one another it is obviously expedient to begin by eliminating the *silver group* by means of hydrochloric acid, which must be added in instalments until the solution is decidedly acid, and, if a permanent pp. appears (which with us can consist only of these three chlorides), until the ppn. is completed.[1] The pp. contains all the silver and mercurosum as $AgCl$ and Hg_2Cl_2, but only part (if any) of the lead; a small quantity of this metal always passing into the filtrate. From the filtrate the copper and arsenic groups are ppd. conjointly by means of sulphuretted hydrogen. Before applying this reagent, however, we must make sure of the at least relative absence of nitrous, nitric, and chloric, acid and other oxidising agents, which, while not easily or completely reducible by H_2S would at least tend to oxidise it and impede its normal action. Any of the three oxidants named can be expelled by repeated evaporation to a *small volume* with conc. hydrochloric acid.[2] The last residue is diluted with the proper proportion of water, and (heedless of any insoluble oxychloride that may separate out) treated with sulphuretted hydrogen, first at about 70° to make sure that As_2O_5 is completely reduced to As_2O_3, and its metal ppd. (as $As_2S_3 + S_2$), and then again after cooling, or else part at least of the cadmium and other copper-arsenic group metals, whose sulphides are rather unstable in opposition to aqueous acids, would escape ppn.

On account of the metals just referred to, we must see that the quantity of free mineral acid is not excessive, but is sufficient to prevent the ppn. of the zinc, which from only feebly acid solutions is liable to pass into the sulphuretted hydrogen pp.

The ppd. sulphides are collected on a filter and washed with very dilute sulphuretted hydrogen water, to constantly re-sulphurise what may have become sulphate by the action of the air; the first instalments of wash-water being acidified to the extent of the mother liquor, to prevent ppn. of the zinc. In order now to separate the two groups, the pp. is digested on a water-bath heat with undiluted *yellow* sulphide of ammonium; an excess of sulphur in this reagent being necessary, chiefly on account of the stannous sulphide, SnS, which becomes soluble only through conversion into stannic, SnS_2. To effect a complete separation, the treatment with sulphide of ammonium may have to be repeated with the first residue. The copper-group sulphides are filtered off and washed with warm water mixed with a little sulphide of ammonium. From the filtrate the arsenic-group sulphides are reproduced by acidification with dilute sulphuric acid; after expulsion of the dissolved sulphuretted hydrogen by a gentle heat, they are filtered off, and washed with plain water (sulphuretted hydrogen water would dissolve sulphide of arsenic As_2S_3). The pp. is liable to be contaminated with sulphide of copper; this can be eliminated by treatment with warm dilute caustic potash, which dissolves the arsenic-group sulphides

[1] If the solution contains Tl, the metal passes for the most part into the pp., where it is easily detected by spectrum analysis. The characteristic solubility of its chloride in Na_2CO_3Aq enables one to separate it from the ordinary silver-group chlorides.

In an *alkaline solution of salts generally*, HClAq may produce a great variety of permanent pps. other than silver-group chlorides. For the purpose of a mere metal-analysis a pretty safe rule is this. If a solution on adding HClAq gives an abnormal-looking pp., repeat the experiment with HNO_3Aq; if no permanent pp. is produced, HClAq will act normally as a chloride; if a pp. is formed, it must be filtered off and analysed for the metals that may be in it, (as sulphides, *e.g.* As_2S_3; or chlorides such as $AgCl$, &c., &c.). The solution, as a rule, is now fit for treatment with hydrochloric acid, &c.

[2] In evaporating a solution of metallic oxides with HClAq, it is as well to remember the volatility of $AsCl_3$, $SbCl_3$, $SbCl_5$, $SnCl_4$, $BiCl_3$. The evaporation is best conducted in a retort, and these volatile chlorides are searched for in the distillate.

GENERIC REACTIONS OF MINERAL-ACID SOLUTIONS OF GROUPS OF METALLIC OXIDES.

Reagents.	Silver Group.	Copper Group.	Arsenic Group.	Iron Group. R″O.	Iron Group. R_2O_3.	Barium Group.	Magnesium Group.	Alkali Group.
	Ag_2O, Hg_2O, PbO.	$HgO, CuO, Bi_2O_3, CdO [PbO]$.	$As_2O_3, Sb_2O_3, SnO, SnO_2$.	FeO, MnO, ZnO, NiO, CoO.	$Al_2O_3, Cr_2O_3, Fe_2O_3$.	BaO, SrO, CaO.	MgO.	$K_2O, Na_2O, [(NH_4)_2O]$.
Hydrochloric acid.	Metals precipitated as chlorides.	METALS REMAIN DISSOLVED.						
Sulphuretted hydrogen and free acid.	Metals precipitated as sulphides, insoluble in largely diluted acid.* Precipitate insoluble in ammonium sulphide.		Precipitate soluble in ammonium sulphide.†	METALS REMAIN DISSOLVED. The following oxides RO_x are reduced to lower oxides RO_y, with precipitation of white *sulphur*, and change of colour. $(RO_x)=Fe_2O_3$ $(RO_y)=FeO$ *Change of colour*: yellow to colourless.		CrO_3 Cr_2O_3 Red to green or violet.	Mn_2O_7 MnO Purple to colourless.	
Ammonium sulphide in neutral or alkaline solutions.	Arsenic Group, no precipitate. The rest precipitated as sulphides insoluble in excess of precipitant.			insoluble in	Cr and Al are precipitated as hydrates; Fe as $Fe_2S_2 + S$.	In the absence of phosphoric, oxalic, and certain other, acids, no visible action.		No change.
Sal-ammoniac and excess of ammonia.	METALS BEHAVE DIFFERENTLY.			Mn, Zn, Ni, and Co, no precipitate.	Fe_2O_3, Al_2O_3, Cr_2O_3 precipitated as hydrates.			
Ammonium carbonate.	METALS BEHAVE DIFFERENTLY.					Metals precipitated as $R''CO_3$ insoluble in NH_4Cl.	In presence of NH_4Cl, no precipitate.	No visible change.
Dilute sulphuric acid.	Hg_2O and PbO precipitated as sulphates.	METALS REMAIN DISSOLVED, even in presence of moderate quantities of alcohol; excepting SnO_2, which may be precipitated.				Ba, Sr precipitated as RSO_4; Ca dil. sol.: no pp.; on addition of alcohol, $CaSO_4$ completely precipitated.	METALS REMAIN DISSOLVED, even in presence of moderate quantities of alcohol.	
Ammonium phosphate, NH_4Cl, and NH_3.	Many of these oxides are precipitated, more or less completely, as phosphates.						Slowly but completely precipitated as $PO_4MgNH_4 + 6H_2O$.	No precipitates.

* As_2O_3 only very slowly precipitated in the cold (more readily when heated), as $As_2S_3+S_2$. † SnS insoluble in colourless $(NH_4)_2S$; but soluble, as SnS_2, in yellow $(NH_4)_2S.S_x$.

only. From the filtrate, these sulphides can be recovered by acidification, in their original form. After elimination of the copper and arsenic groups, the *barium-group* may be separated out by means of sulphuric acid. The barium comes down at once (as $BaSO_4$), the strontium gradually, on standing and keeping warm. From the filtrate from these two sulphates the calcium can be ppd., after due concentration, by judicious addition of alcohol, and allowing to stand for, say, 12 hours. The calcium sulphate is filtered off and washed, first with dilute, and lastly with strong, alcohol. The filtrate, after removal of the alcohol, is ready for the elimination of the iron-group, &c. This method is the best that can be adopted if an analysis for the barium-group metals is our principal object; it also offers certain other specific advantages; yet the majority of chemists prefer (after application of sulphuretted hydrogen in the presence of acid) at once to separate out the *iron-group*, by means of sulphide of ammonium. The addition of this precipitant must of course be preceded by the neutralisation of the free mineral acid of the solution with ammonia; if a sufficiency of sal-ammoniac is not thus produced incidentally, some sal-ammoniac must be added, to bring the pp. into a fit condition for filtration. But we have no space for these technicalities, and accordingly assume the pp. to have been filtered off and washed with warm water mixed with some sulphide of ammonium, so as to remove the whole of the mother-liquor. This liquor, by theory, contains the whole, in practice it may be assumed in general to contain the bulk, of the barium-group metals and of the magnesium, in addition to the whole of the alkalis. For its analysis, the barium-group is ppd. by means of carbonate of ammonia added to a warm solution. In the presence of ammonia-salts, of which as a rule there is more than enough, only the barium-group metals are ppd. as carbonates; the pp. is collected on a filter, and washed with hot water. Part of the filtrate serves for the detection of magnesia by means of ammonium phosphate. The rest of the filtrate is evaporated to dryness, and the residue calcined. The ammonium-salts volatilise, or at least their ammonia does, and there remains a residue containing only magnesium and alkali-metals, which latter can be detected without elimination of the magnesium by suitable methods.

In regard to the analysis of the groups, our space does not permit us to do more than shortly indicate how the *sulphide of ammonium* pp. (which may be of very complex composition), can be split up into minor groups. Before doing so, let us state that in the presence of representatives of a certain group of acids which includes H_3PO_4,HF,H_3BO_3, and certain organic acids, *e.g.* oxalic, the pp. is liable to contain part, or all that there is, of barium-group metals and of magnesium, as salts of the acids named. A thoughtful analyst takes care to keep these inconvenient acids out of the solution; but the introduction of phosphoric acid is often unavoidable, and we therefore assume it to be present. Whether this acid is present or not, the *cobalt and nickel* can be eliminated, approximately at least, by treatment of the pp. with cold, dilute[1] HClAq, and removed by filtration. The filtrate is next tested for iron, best by adding a few granules of chlorate of potash and boiling, when the iron assumes the form of ferric salt, and becomes visible by the intense yellow colour of its hot hydrochloric solution, and at the same time assumes the right form for the next step, which aims at a separation of the metals present as Fe_2Cl_6, Al_2Cl_6, Cr_2Cl_6, and the phosphates, from the metals (manganese, zinc, &c.) present as dichlorides. Of the various methods which we have for their separation, the most convenient for general purposes is the following:—

After having made sure of the complete reduction of the manganese (Mn_2Cl_6) to manganous chloride by sufficient boiling with hydrochloric acid, we allow to cool, dilute pretty considerably, and next add (sal-ammoniac if necessary, and) ammonia, drop by drop, until the mixture is alkaline. We then (without losing time and giving the oxide of manganese much chance to get per-oxidised), boil until the vapours cease to smell of ammonia, and filter. The pp. contains all the iron, aluminium, and chromium, and all the phosphoric acid as lime-salt, or in other forms; the filtrate contains at least part of the zinc, manganese, and in general part of the rest of the protoxides. If the sesquioxide-pp. is bulky, it must be re-dissolved (after a few washings) and re-produced by a repetition of the first operation. From the *protoxide* filtrate, the zinc, after acidification with acetic acid, can be ppd. pure by fractional ppn. with sulphuretted hydrogen-water in the cold. The manganese, traces of nickel and cobalt, and in general much lime, baryta, and strontia, remain dissolved.

The *sesquioxides*-pp.[2] (if chromium be pre-

[1] *The cobalt-nickel* pp. never contains the whole of these metals; part passes into solution, and ultimately finds its way into the '*protoxide filtrate.*' In addition to its normal components it is liable to contain sulphide of zinc, and perhaps traces of other iron-group metals, and any cadmium, antimony, &c., that may have been allowed to slip into the filtrate from the sulphuretted hydrogen pp.

[2] If the solution contains *uranium*, this, in our scheme of analysis, goes with the iron, and consequently has to be looked for in the *sesquioxide* pp.; from which it can be extracted by digestion with warm, concentrated, solution of carbonate of ammonia. To pass now to a number of rare metals, which we have so far entirely ignored:

Palladium, in our system, belongs to the copper-group. It is characterised chiefly by the utter insolubility and black colour of its iodide.

Platinum and gold go into the arsenic group; only the sulphides are not easily soluble in alkaline sulphides. In almost all practical cases they can be kept outside the solution intended for the detection of the metals by suitable methods. If they are unavoidably present, they are best separated out; the gold by ferrous chloride (as metal); the platinum, by means of *solid* sal-ammoniac added to the concentrated solution, as $PtCl_6(NH_4)_2$, which must be washed with the least possible quantity of a solution of the precipitant.

Titanium, as TiO_2, in the analyst's sense stands between SiO_2 and Al_2O_3. In our system it goes with the Al_2O_3.

Beryllium behaves to our group-reagents like Al_2O_3, but it is far more easily soluble in sal-ammoniac than alumina is. Unlike it, it dissolves in carbonate of ammonia, and does not form an alum.

The rare earth metals, cerium, lanthanum, &c., &c., must all be passed over here.

Lithium (easily detected by spectrum analysis) behaves on the whole like K and Na, but unlike them forms an insoluble phosphate producible by evaporating its solution with phosphate of soda plus caustic soda (*i.e.* with Na_3PO_4), to dryness, and treating the residue with water, when it remains. From magnesia (if ammonia salts are absent) it

sent) is best analysed by fusion with caustic potash and nitre in a silver dish, and treatment of the fused mass with water. Should the solution be green from manganate, this must be reduced (to MnO_2) by addition of a few drops of alcohol and heating. The mixture is then filtered. The *filtrate* contains the chromium as (yellow) chromate, the aluminium as aluminate, and part, in general, of the phosphoric acid as phosphate. The *residue* contains oxide of iron, magnesia (MgO), and possibly barium-group metals as phosphates.

The Determination of the Non-Metallic Components.—Our systematic methods for the detection of the metals contained in a solution of salts are far less hampered by onerous conditions than are most of our methods of acid detection. Hence the general rule to first complete the analysis for metals before attempting the systematic and exhaustive search for the non-metallic components. How far the solutions obtained in the disintegrations are available for the latter purpose, and the respective methods of procedure generally, depend chiefly upon whether we merely aim at the detection of the non-metallic elements as such or at that of the acid radicles contained in the substance. All we could say in regard to the former case is anticipated in the section on the '*Detection of certain elements, &c.*' (p. 217) and the latter is not susceptible of being treated instructively in general terms. In regard to it we must refer to the special hand-books.

Quantitative Analysis.

The general problem of quantitative analysis defines itself. Its, solution, scientifically at least, assumes its simplest form, if the thing to be analysed is given as a free substance and the (let us say *one*) component to be determined can be separated out exhaustively in the form in which it is meant to be reported. In such a case all that is required, in addition to the analysis proper, is the numerical definition of the two quantities concerned. Of the several direct methods which we have for this purpose, only two need be mentioned; one is to measure the *volume* of the body under stated conditions of temperature and pressure, the other is to determine its *weight*. The former method is confined in practice to gases and liquids; the latter is applicable, and indeed is applied, to bodies of all kinds, and, when we have choice, applied preferably. The volume of a body is a function of temperature and pressure, and its numerical statement is consequently encumbered with the necessary reference to—in general—two corresponding standards; the weight of a given body depends only on the intensity of gravity, and even this variable in practice is out of court, because, in chemistry we always use that well-known method of relative weighing which measures the weight of the body not in terms of a unit-force but as a multiple of the weight, at the time and place, of an adopted standard mass, viz. the unit-piece of our set of weights. The result of such a weighing is independent of the prevailing force of gravity, and consequently not subject to any variation; it consequently, at least, *indexes* the mass with perfect definiteness. We, moreover, know that it is independent of any chemical change within the body (or set of bodies) weighed. A mass of, for instance, sulphide of copper weighs precisely as much as the two components did conjointly. Hence for chemical purposes our method of weighing might safely be viewed as a method of true mass-measurement, even if Newton had not proved that equal weights (chemically determined) correspond to equal *inertias*.

The method of direct quantitative analysis explained is the only one which suggests itself when the component to be determined is a chemically indefinite mixture (such as for instance the mixture of salts contained in a natural water); it applies to a good many other cases; but of course breaks down whenever the body to be determined is an imaginary radicle such as SO_4 or ClO_3, &c. In such cases (and many others as a matter of expediency) we determine the component by one or other of our indirect methods of mass measurements; which, however, all come to this, that instead of the unknown mass x, we measure some other quantity q, which bears to x a known fixed relation, $x=f(q,m)$, where m is a mass which must be measured directly, although the analyst does not always do this at the time, or himself at all.

Most of our determinations in analysis are uncertain by at least 0·001 of their values, and a higher degree of relative precision is afforded by any fair ordinary balance. But the nature of our methods compels us, in general, to work on small quantities—we rarely care to start with more than one gram of a given solid—and besides the products to be weighed can in most cases not be placed on the bare pan, but must be shut up in apparatus weighing perhaps 100 or 1000 times as much as themselves. The net weight then comes to us only as a small difference between two large weights directly determined. So it comes that even for the ordinary routine of quantitative analysis, we need a balance which to be generally useful should carry about 100 grams on each side, and with this charge turn distinctly with anything greater than, say, 0·2 milligrams.

The Chemical Balance.[1]

In its present form the chemical balance is nothing more than a refinement upon the ordinary beam and scales to be seen in any grocer's shop; it is a more perfect realisation of the same ideal machine. There is an absolutely rigid beam, suspended so that while it oscillates freely about a certain axis, every *point* of which is *fixed* in reference to the stand, it cannot perform any other motion. From two points which lie in the same plane with the axis of rotation—one A near the left, the other B near the right, end,—the pans are suspended by means of absolutely flexible linear strings. A and B are equidistant from the axis of rotation. The form of the (ideal) beam is arbitrary; so in

is separated by solution of baryta in a warm liquid which pps. only the magnesium as $Mg(OH)_2$.

Rubidium and cæsium, in any scheme of analysis, follow potassium to the end.

[1] Partly abstracted from the writer's memoir: *Ueber die Waage des Chemikers* (*Zeitschrift für Instrumentenkunde*, 1881, 313 *et seq.*).

a sense is its mass, which, however, must be so distributed that, supposing the line A B to be horizontal, the centre of gravity of the empty beam lies vertically below, though very near, the axis of rotation. Let us at once add that in the actual instrument the weight of the beam should be no greater than is necessary to ensure to it sufficient stability of form in all circumstances, because the greater the weight of the beam, the greater (*cæt. par.*) the friction in the axis of rotation, and the greater the time of vibration.

Of the difficulties involved in realising the ideal machine, that of producing a light and yet practically inflexible beam seems to have rested most heavily upon the minds of the earlier makers; but there can be no doubt that many of their efforts in this direction (which occasionally resulted in what we should now call fantastical beam forms, such as hollow ellipsoids or double cones, monstrous skeleton forms, &c.) must be traced back to their inability to reach a sufficient degree of precision in the geometric adjustment of the three pivots, and their thus charging against the flexibility of the beam what was really owing to these defects in the adjustment. As these difficulties were overcome, beams assumed less fantastic forms. Sacré, of Brussels, we believe, never uses any but plain rod-shaped beams for even his finest instruments; most balance-makers, however, prefer the form of a largely perforated rhombus or flat isosceles triangle; and thereby attain all that is needful even for the best instruments without offending the eye by unduly stretching the maximum section, or without using anything more rigid, intrinsically, than hammered brass or some kind of hard bronze.[1]

In all modern balances the *axis of rotation* is sought to be realised in a straight knife-edge ground to a prism of hard material, which is firmly fixed to the beam traversing it cross-wise, and rests—in the best balances along its entire length – on a horizontal, plane, (and equally hard) bearing fixed to the stand. The arrestment is so contrived that, besides doing its primary duty, it secures to each point of the knife-edge a fixed position on its bearing whenever the balance works. In former times both bearings and knives used to be made of hard steel; subsequently agate bearings came to be combined with steel edges, and this is still the most popular combination; although Robinson long ago introduced agate knives in conjunction with agate bearings. The agate knife adds nothing to the precision or mechanical durability, but for laboratory balances offers the great advantage of rendering the system proof against acid-vapours; accordingly it is gaining more and more in popularity. Quite lately an American has introduced as a material for both knives and bearings that very hard (and acid-proof) alloy of osmium and iridium which is used for the tipping of stylograph pens.

The point pivots, A and B, used to be realised visibly by means of two circular knives fixed to the end of the beam so that their working-edges were parallel to the axis of rotation. From the lowest points, the pans were suspended by means of ? shaped hooks of steel wire. In this way a very high degree of precision can be attained, and the system when well executed is more durable than one would think, but with balances used for heavy charges it cannot possibly last for many years.

In the better system introduced by Robinson of London half a century ago each extremity of the beam is provided with a knife-edge similar to the central one (except that it is turned upwards); on each knife-edge rests a stirrup-shaped (or J-shaped) contrivance, terminating in a ring below, and from this ring the pan is suspended by a hook. This, of course, comes to the same as if the pan were suspended from the projection of the working point of the hook-and-eye arrangement on the respective knife-edge; so that the latter need not be absolutely parallel to the axis of rotation. Flat end-bearings demand a somewhat cumbrous and expensive appendage to the arrestment to secure to each point of every edge a fixed position on its bearing in the working instrument. Hence Staudinger, and many others, prefer to combine (long) end-knives with roof-shaped bearings, which, in virtue of their shape, fall into their prescribed positions without external aid.

In now passing from fundamentally important to subsidiary points, the *arrestment* ought to be taken up first; but we could not possibly do justice to this (practically all-important) subject without workman-like drawings and lengthy descriptions. We therefore pass on at once to the *needle* which serves to define the position of the beam in reference to the plumb-line.

In the precision-balance the needle is made to point downwards towards a scale fixed to the lowest convenient point of the pillar. The zero-point defines the 'normal position' of the beam, *i.e.* that position in which its centre of gravity lies vertically below the axis of rotation. The scale is so divided that the radii drawn from the axis of rotation through the marks divide the tangent to the circle described by the oscillating needle, at the zero point, into pieces of equal length, which in most practical cases means into degrees of equal angular value.

To avoid the use of small weights, each arm of the beam, in most balances, is divided into ten equal parts in the sense that the projections of the marks on the line A B connecting the two point-pivots divide the distance from the central pivot to (say) B into ten equal parts. A rider weighing ten mgms., when suspended on mark 1, 2, 3, &c., acts like 1, 2, 3, &c., mgms. placed on the pan. In most balances, however, points 0 and 10 are inaccessible. Becker's Sons, of Rotterdam, avoid this inconvenience by dividing each arm into twelve equal parts, and providing a rider of twelve mgms. weight. Some makers make the top bar of their beams straight, and exactly parallel to the plane of the three pivots, and let it project beyond the terminal edges, besides keeping it clear of encumbrances, so that the rider can move freely from one end of the beam to the other. This system, besides its obvious advantages, admits of the use of heavier riders; because the increase in sensibility caused by the presence of the rider is the same at any position which it may have; only the

[1] For further information regarding this question we refer to the writer's memoir quoted in footnote to p. 223.

rider in such cases must be counted part and parcel of the instrument.[1]

In proceeding now to develop the statical theory of the precision-balance we will assume, for a first approximation, that the three pivots are physically and geometrically perfect in themselves, but, for the sake of greater generality, we will not assume that the knives are exactly in their intended positions. Imagine a system of rectangular co-ordinates fixed to the beam so that, while the Z-axis coincides with the axis of rotation, the X-axis goes through the centre of the middle knife, and runs parallel to the line A B which joins the two point-pivots. Let the co-ordinates of A and B, of the centre of gravity S_0 of the empty beam, and of a certain point C to be defined presently, be as follows:

	A	B	S_0	C
$x=$	$-l'$	$+l''$	o	x_0
$y=$	$+h^*$	$+h^*$	s_0	y_0

Let P′ denote the total charge from A, P″ that from B, and W_0 the weight of the empty beam; the joint effect of these three weights is the same as if they were all concentrated in some point C at $x=x_0$ and $y=y_0$. For calculating purposes we may assume gravity in one case I. to act in the direction of the Y-axis, and in a second II. in the direction of the X-axis; we then have:

(Case I.) $\quad P''l''-P'l'=(P'+P''+W_0)x_0 \quad$ I.

(Case II.) $(P'+P'')h+W_0s_0=$
$$(P'+P''+W)(P'+P''+W_0)y_0 \quad \text{II.}$$

In any sensibly constructed balance things are so arranged that, under all circumstances that come into practical consideration, the centre of gravity C of the whole system lies outside and below the axis of rotation (*i.e.* that $y_0>o$). Assuming both x_0 and y_0 to have positive values, and the beam to be left to itself in its normal position, it will turn, and tend to assume that position in which C lies vertically below the axis of rotation. The radius OC then describes an angle equal to that which separates OC from the Y-axis, and obviously,

$$\tan.\ \alpha=\frac{x_0}{y_0}=\frac{P''l''-P'l'}{(P'+P'')hW_0s_0} \quad . \quad . \quad \text{III.}$$

To bring the equation into a handier form for our purposes, let us separate P′ and P″ into parts, thus; $P'=p'_0+p'$, and $P''=p'_0+p''$ where the p_0s stand for the weights of the empty pans, which are always so adjusted that $p'_0l'=p_0''l''$; let us then lump $p'_0+p''_0$ with the weight of the beam as $W=W_0+p'_0+p''_0$ and write

$$\tan.\ \alpha=\frac{p''l''-p'l'}{(p'+p'')+Ws} \quad . \quad . \quad . \quad . \quad \text{IIIa.}$$

where s has an obvious meaning. We then have for x_0 the equation

$$p''l''-p'l'=(p'+p''+W)x_0.$$

This equation may be said to state the theory of the ordinary method of weighing. To find the weight p' of a given body we place it on the left pan, and then try heavier and lighter combinations of standards on the right, until we have found out that one (representing p'' grams) which reduces x_0 to nothing, so that the balance is at rest at, or it vibrates about, its normal position. We then have $p'=\frac{p''l''}{l'}$.

In formulating the relation between a small overweight on one side and the corresponding angle of derivation α, we may take $l'=l''$ (as it really is very nearly in all well-adjusted balances), and (for $p'=p$ and $p''=p+\Delta$) write

$$\tan.\ \alpha=\frac{\Delta l}{Ws+2ph} \quad . \quad . \quad . \quad . \quad . \quad \text{IV.}$$

where α means the angle through which the position of rest turns in consequence of the addition of Δ units of weight to the right pan, the charge before having been $x=p$ on each side.

In practice tan. α is measured in degrees of the scale. Supposing α corresponds to n degrees of the scale, and the index-length is J in degrees, we have

$$\frac{n}{J}=\frac{\Delta l}{Ws+2ph} \quad . \quad . \quad . \quad . \quad \text{V.}$$

The ratio $\frac{n}{\Delta}$ defines the *sensibility* of the balance; we have for it

$$E=\frac{n}{\Delta}=\frac{l\,J}{Ws+2ph} \quad . \quad . \quad . \quad . \quad \text{VI.}$$

and for its reciprocal, $\frac{1}{E}$, the weight-value of 1° of the scale,

$$\frac{1}{E}=\frac{Ws+2ph}{l\,J} \quad . \quad . \quad . \quad . \quad \text{VII.}$$

For $h=0$, the term $2ph$ vanishes, and the sensibility becomes independent of the charge. In the actual instrument h is a function of the charge, of the form $h=h_0+\beta p$, where β is a small constant depending on the coefficient of elasticity and the configuration of the beam. For a given charge, a good maker has no difficulty in bringing h down to less than $\pm 0{\cdot}01$ mm. The best instruments are so adjusted that, for a certain medium charge, $h=0$, so that for $p=0$ it has a small negative, and from $p=$ maximum charge a small positive, value. The relative change in the sensibility involved in passing from $p=0$ to $p=p$, is shown by the equation

$$\frac{E^{-1}-E_0^{-1}}{E_0^{-1}}=\frac{2ph}{Ws}$$

and consequently is the less (*cæt. par.*), the greater s, *i.e.* the less the initial sensibility, E_0. It (*i.e.* the left side of our equation) comes to its minimum (assuming p to represent the maximum charge) if the balance is so adjusted that, for the charge $0{\cdot}83\ p$, $h=0$. Supposing this rule to be generally adopted, the relative inconstancy of the sensibility is independent of the arm-length (see the writer's memoir, p. 318).

No balance is complete without a 'gravity-bob,' a small button or sphere of metal attached to a wire which stands vertical on the top of the beam (in the Y-axis) so that it can be screwed up and down into any position. Matters are arranged so that when the bob is quite down the sensibility is below the lowest value we care for, while, by screwing up the bob to its highest place, we can bring C into, and even a little to the wrong side of, the axis of rotation. Hence it would appear that, by screwing up the bob sufficiently we can get our balance to turn

[1] For more exact information see the writer's memoir, page 322.

* + means 'below x.'

visibly with say 0·001 milligram or anything less that we might care to name. So indeed it would be if our fundamental assumptions could be—and were—realised. In practice, however, the knife edges are *not* absolutely straight nor the bearings absolutely plane, and neither are absolutely rigid. Hence the three axes, instead of being always at $x = \text{A}$, o, B respectively, so to say oscillate irregularly, each from $x - \lambda$ to $x + \lambda$, where x is the theoretical x. In going more fully into the matter we see that as a consequence the balance at a given charge (say p left; p right) is in a state of indifferent equilibrium within a small angle $\pm\beta$, which, of course, is the greater the greater is E. But the weight-value ϵ of this angle is constant, and is governed by *some* equation *like*

$$\epsilon = \frac{\lambda}{l}(\text{w} + 2p)$$

where 'λ' is meant to lump the joint effect of the three λs previously referred to. ϵ may be called the 'inherent error' of the balance. There is obviously no use in screwing up the bob any further than necessary to render this ϵ (*i.e.* angle β) distinctly visible. It may be inexpedient even to go so far, because, in practice, we never aim at the absolutely true weight, but at a value sure to differ from it by no more than say $\pm 0{\cdot}1$ mgm. The angle corresponding to this need not be more than distinctly visible. To make the angle greater than necessary needlessly adds to the time of vibration which may already be inconveniently high. Because the time of vibration (t in seconds) is governed by the equation

$$t^2 = \frac{l^2\,\{\,k\text{w}_0 + 2(p_0 + p)\,\}}{R\,\{\,\text{w}_0 s_0 + 2(p_0 + p)h\,\}} \qquad . \quad . \quad \text{VIII.}$$

where R denotes the length of the pendulum beating seconds at the place of observation. $k\text{w}_0 l^2$ denotes the *momentum inertiæ* of the empty beam in reference to the axis of rotation. The denominator of eq. VIII. suggests the expression given in eq. VII. for the sensibility E. Combining the two we have

$$t^2 = \frac{l}{\text{RJ}}\,\{\,(k\text{w}_0 + 2p_0) + 2p\,\}\,\text{E} \qquad . \quad . \quad \text{IX.}$$

The bob enables us to choose our own E. or our own t (for a named charge), but it does not enable us to choose both. We of course refer to a ready-made balance; in the hands of a mechanician who designs a balance for a stated purpose, l becomes an arbitrary variable, and the equation then assumes something like this form :

$$t^2 = l(\text{c} + kbl + 2p)\,\text{E} \qquad . \quad . \quad . \quad . \quad . \quad \text{X.}$$

where c and b are constants whose meaning is sufficiently apparent. In words: Whatever (reasonable) value for E may have been fixed upon we can bring down t (for say $p = 0$) to any desired figure by making l sufficiently small. But where shall we stop? For high-class balances intended to weigh up to 100 grams, mechanicians used to draw the line at $l = 180$ to 200 mm. These values (perhaps more by dint of habit than on rational grounds) were retained until about twenty years ago, when P. Bunge, of Hamburg, introduced a new form of the instrument, in which the arm-length is reduced to some 60 to 65 mm. Thanks to the general excellence of Bunge's work, these short beams soon became very popular among both chemists and mechanicians; and it therefore is worth while to inquire what their specific advantages as short-beam balances amount to.

For this purpose the writer, some years ago, determined the constants of eq. X. for a very excellent Oertling (hectogram) balance, which he has in his possession, (its $l = 184$ mm.), and, taking it as a general model for an imaginary genus, calculated the values of t for a number of charges and sensibilities, assuming l to be equal to (a) 180 mm. and (b) 60 mm. He found for

I. E = 2 *degrees of the scale per* 1 *mgm. of over-weight.*[1]

if $l =$	180 mm.	60 mm.
for $p = 0$; $t =$	7″·7	3″·6

The short beam obviously vibrates too fast for high-precision work. To set this right let us screw up the bob on both sides, so as to double the sensibility. We now have

II. E = 4 *degrees per mgm.*

if $l =$	180 mm.	60 mm.
for $p = 0$; $t =$	11″·0	5″·2
as $p = 30$; $t =$	14″·8	7″·8
as $p = 100$: $t =$	21″·2	11″·6
$t_{100} : t_0 =$	1·93	2·23

The times of vibration no doubt assume the more convenient values in the shorter beamed instrument. But what does this amount to practically? In our opinion not to as much as some people seem to think. We are inclined to think that the short beam offers material advantages to those who are accustomed to the *dead-beat* method of weighing (see below). All those who prefer the method of vibration will on the whole, we think, fare better with the old form of the instrument. But this, to be complete, should be provided with the two following auxiliary contrivances of the writer's invention:

I. *An auxiliary small bob*[2] attached by mere friction to the upper part of the needle, which has the form of a triangular prism and is (virtually or actually) graduated, so that one is able, at a moment's notice, to give to the weight-value of 1° of the scale any convenient pre-determined value, to make it equal to exactly 2, 1, 0·5, 0·2 &c. mgm. as he may please.

II. *A microscopic arrangement*[3] for reading the excursions of the needle. A narrow ivory scale, divided into very small degrees, is fixed to the needle near its lower end, so that a microscope which is fixed slantingly to the stand but passes through the central (fixed) portion of the front pane enables one to read it. The microscope has a vertical wire in its focus; this wire appears as a vertical line crossing the image of the scale. Every degree of the micro-scale corresponds to exactly 0·1 degree of the ordinary scale, which latter does duty as usual. As the microscope reverses the image, the apparent motion of the 'wire' on the micro-scale is in the

[1] *I.e.* the addition of 1 mgm. causes the needle to oscillate between 0 and ± 2°; 1° in the given instrument = 1 mm. very nearly.

[2] Pr. E., 1876; *C. N.* 33, 157.

[3] *Zeitschrift für Instrumentenkunde*, 1882, p. 63.

same sense as the real motion of the needle in reference to the ordinary scale, so that there is no fear of blunders through mistaking plus for minus. The writer is indebted to Mr. Oertling for having executed this arrangement for him in a most masterly manner. Though intended originally to be reserved for special work, such as weight-testing &c., it was found so convenient that both the writer and his assistants use it preferably for even their everyday weighings. The specific advantage of the microscope is that it enables one to adjust the 'bob' so as to produce the most convenient time of vibration. The microscope more than makes up for the involved loss of sensibility.

On Weighing.

A precision-balance should stand on an unshakable table, and should not be exposed to the risk of one-sided elevation of temperature. Before being used for a series of weighings it must of course be set in order, which includes that the case be 'levelled,' so that the plane including the axis of rotation and the zero of the scale is a plumb-plane. The next thing to do (if necessary) is to bring the 'bob' into its proper position; *i.e.* to place it so that the least difference of weight we care for just becomes visible as an angle of deviation and no more, because to increase the sensibility beyond what is needful means needlessly to diminish the range of weights determinable by vibration, the constancy of the sensibility, and the rate of vibration. This rate of course must not be allowed to fall below a certain limiting value. In the writer's opinion, $t = 5''$ is about the lowest permissible limit for relatively heavy charges. Next, the balance must be brought 'into equilibrium' at least approximately. For this purpose Oertling's balances carry a vane at the top of the beam, consisting of a little lever hinged to the wire of the bob, which can be turned round, so as to shift the centre of gravity to the right or left.[1] A better arrangement is a small horizontal gravity bob at one end of the beam. For simplicity's sake we assume that the balance has been brought into perfect equilibrium, so that the needle in the vibrating instrument moves forwards and backwards between $+n°$ and $-n°$. To weigh an object (which, to fix ideas, we will assume to be a solid, and non-hygroscopic), the ordinary mode is to place it on the left pan, and then counterpoise very nearly with standard weights, say p grams, on the right. In order now to determine the small additional weight which is required to establish perfect equilibrium, we may use one or other of two methods. In the

Dead-beat method we simply continue our trials, until the needle vibrates about the zero as its position of potential rest. It is, however, hardly possible for any thinking person to use this method without at least instinctively combining it with

The method of vibration, which in its most exact form consists in this that we note down (at least mentally) the successive excursions of the needle, and from these calculate the position of rest. Supposing we count distances traced by the needle in moving from 0 to the left as positive, and those to the right as negative, and the needle turns successively at n_1, n_2, n_3, n_4, n_5, degrees, we have for the position of rest, 4 values,

$$\tfrac{1}{2}(n_1+n_2);\ \tfrac{1}{2}(n_2+n_3);\ \tfrac{1}{2}(n_3+n_4);\ \tfrac{1}{2}(n_4+n_5),$$

and the mean of these four values gives the reading corresponding to the position of rest. But the factor $\frac{1}{2}$ can be dropped, because we are evidently at liberty to measure in half-degrees. By taking an odd number of readings we eliminate the error caused by what the needle loses in passing through its path; for ordinary practice 3 readings are sufficient. It suffices to determine $n_1 = (\text{say}) + 4{\cdot}2$; $n_2 = -1{\cdot}0$; $n_3 = +4{\cdot}0$, and compute 'a' = mean of $+3{\cdot}2$ and $+3{\cdot}0 = +3{\cdot}1$. In this case the right pan is too heavy by $3{\cdot}1 \times k$ mgms., if k is the weight-value of 1° at the respective charge. In a good balance k is almost independent of the charge; the writer's supplementary bob of course enables one to give it a pre-determined value. How k is determined need not be explained.

Supposing p grams to have established exact equilibrium, the object weighs

$$x = p\,\frac{l''}{l'}\ \text{grams}.$$

The several weights which enter the calculation of an analysis need only be relatively correct. Hence, if all the weighings involved are made on the same balance and with the same set of weights, and the objects are always in the left pan, in any such series we may adopt $\frac{l''}{l'}$ grms. as our unit and say $x = p$.

We do not consider it necessary to quote examples of cases in which as a matter of principle $\frac{l''}{l'}$ dare not be cancelled; we rather say that in all precision-balances worthy of the name $\frac{l''}{l'}$ is *very* small, not more than 0·00005 at the most. If the empty balance was in equilibrium at $+a_0$ degrees we must add, if at $-a_0$ degrees we must subtract, a_0k mgms. from p.

Absolute Weighing.

Absolute precision-weighing in the chemical laboratory hardly occurs otherwise than in this sense that we may have to determine the weight of an object in terms of an *arbitrary* (but for this occasion absolute) standard. For this we have two methods.

I. *The Method of Substitution.* The object is placed in one pan of the balance, and counterpoised exactly by some suitable tare placed in the other. We then take off the object and put on standard weights until equilibrium is again established. If the method of vibration be used, the immediate result is the proof that the constant tare was balanced by (1) x grams of object plus δ grams, and (2) by $p + \delta_2$ grams of standards. Whence $x = p + \delta_2 - \delta_1$.

II. *The Method of Reversion.* After having brought the balance very nearly into equilibrium, we ascertain the number of grams which have to be placed in the opposite pan to exactly

[1] A vane with properly graduated limb is as good as a 'rider'; better in fact, inasmuch as it is not liable to drop off and get lost; this innovation was proposed by Hempel, but has not met with much favour as far as we know.

balance the object, once with the object on the left, and once with the object on the right, side. Assuming, for greater generality, that the right pan was from the first too heavy by δ grams, we have

I. $xl' = (p'' + \delta)\, l''$ by the first trial.

II. $(x + \delta)\, l'' = p'l'$ by the second trial.

Assuming for a moment that $l' = l''$ (as we always may if x is small), we obviously have $2x + \delta = p' + p'' + \delta$; or $x = \frac{1}{2}(p' + p'')$.

We will now drop this assumption, but assume that δ is so small that the balance cannot distinguish between $\delta l'$ and $\delta l''$; then we may write as

$$\text{I. } (x - \delta)\, l' = p''l''.$$
$$\text{II. } (x + \delta)\, l'' = p'l'.$$

Whence, by multiplication,

$$p'p'' = (x - \delta)(x + \delta) = x^2\left(1 + \frac{\delta}{x}\right)\left(1 - \frac{\delta}{x}\right) = x^2\left(1 - \frac{\delta^2}{x^2}\right).$$

It is always possible to make a guess at the maximum value which $\frac{\delta^2}{x^2}$ could possibly have; supposing $\delta = \pm 0{\cdot}001$ grm. and x (*i.e.* p' or p'') = about 10 grms. $\delta^2 \div x^2 = 1 \div 10^8$ and can be neglected. In practice we take care not to allow δ to assume a greater relative value, and compute by $x^2 = p'p'$ or $x = \sqrt{p'p'}$, for which expression we may substitute $\frac{1}{2}(p' + p'')$, if p' and p'' differ by less than, say, p mgms.

On Sets of Weights.

A set of weights to be fully on a par with a given balance must be so exactly adjusted that no combination of the several pieces which can ever occur is wrong by more than the inherent error 'ϵ' (*v. supra*) of the instrument. This means that chemical weights, to be properly adjusted, require a balance of a very high order. But even the most perfectly adjusted set is of no permanent value unless the substance that it is made of offers a sufficient guarantee for constancy of mass. Of all available materials, rock-crystal comes nearest perfection, but it is difficult to work and bring into a handy shape. Of metals, Mr. George Matthey's ten per cent. iridio-platinum is the best; it is absolutely proof against even acid fumes, and sufficiently hard to be proof against abrasion by reasonable usage. Next after it comes 'hard' platinum (the slightly iridiferous metal of which crucibles are generally made); pure platinum is too soft. Brass, bronze, German silver, and other cheap metals are mere apologies for what ought to be used; yet these are used (in a sense unavoidably) for making the larger pieces in sets for every-day use. Gilding affords no protection against atmospheric influences, unless the noble metal is laid on thickly; a good lacquer is better than the film of gold which is customarily put on by electrolysis.

In constructing a set of chemical weights, we might choose our own unit, but whatever unit we might fix upon, any other mode of subdivision or multiplication than the decimal mode would be absurd; and there is no reason why we should not adopt some legally fixed and universally obtainable unit as *our* unit. The gram is used by chemists all over the world, almost to the exclusion of any other unit.

Sets of weights exact enough for all practical purposes can be had in commerce. Whoever may be the maker, a set of weights should not be used without having first been tested and found correct, at least in a relative sense. To show how the errors in a given set can be determined, let us assume for a while our set comprised only the pieces $(1)_0$, (1), (2), $(2)_1$, (5), (10) grams, and adopt these bracketed numbers as symbols for the unknown true weights. As a unit for the errors to be determined, we will adopt the 1 milligram as determined by a given rider of 10 mgm. weight; the $(1)_0$ shall serve as our provisional unit for the values (1) (2) (10). To determine (1) we compare it with $(1)_0$ by the method of substitution or reversal, and note down the difference between the two in terms of 'the milligram,' as determined by the method of vibration. We then compare $(1)_0 + (1)$ with (2); then (2) with $(2)_1$, &c., &c., to establish the following equations:

$$
\begin{array}{lll}
(1) & = (1)_0 + \delta_1 & \text{mgms.} \\
(2) & = (1)_0 + (1) + \delta_2. & \text{,,} \\
(2)_1 & = (2) + \delta'_2. & \text{,,} \\
(5) & = (2) + (2)_1 + (1)_0 + \delta_5. & \text{,,}
\end{array}
$$

$$
\begin{array}{llr}
 & & \textit{Computed.} \\
(1) & = (1)_0 + \delta_1 \quad . \quad . \quad . & (1)_0 + \Delta_1 \text{ mgs.} \\
(2) & = 2 \times (1)_0 + \delta_1 + \delta_2 \quad . & 2 \times (1)_0 + \Delta_2 \quad \text{,,} \\
(2)_1 & = 2(1)_0 + \delta_1 + \delta_2 + \delta'_2 \quad . & 2 \times (1)_0 + \Delta'_2 \quad \text{,,} \\
(5) & = 5(1)_0 + 2\delta_1 + 2\delta_2 + \delta'_2 + \delta_5 & 5 \times (1)_0 + \Delta_5 \quad \text{,,} \\
(10) & = 10 \times (1)_0 + \text{ \&c.} \quad . & 10 \times (1)_0 + \Delta_{10} \quad \text{,,}
\end{array}
$$

To know what the values $n \times (1)_0$ really are in terms of an adopted gram (say the true gram) we must compare one of the pieces, or a combination of some or all, directly with the corresponding standard weight. Supposing this had been done with the 10 gram piece, and this piece had been found free of error, we have $10 \times (1)_0 + \Delta_{10}\text{mg.} = 10\,\text{g.}$ (meaning 10 true grams)

$$\therefore (1)_0 = \frac{10\,\text{g.} - \Delta_{10}\,\text{mg.}}{10} = 1\,\text{g.} - \frac{\Delta_{10}}{10}\text{mgs.}$$

and by substituting this value for $(1)_0$ in the expressions $n \times (1)_0 + \Delta_n$ we obtain the values of all the six pieces in the form

$$(\text{N}) = \text{N g.} + x \text{ mgm.};$$

but our 'mgm.' is strictly speaking an arbitrary unit; we have no right, for instance, to say

$$(5) = 5\,\text{g.} + \frac{x_5}{1000}\,\text{g.}$$

What the true gram-value of the rider is can only be found by joining on to our gram set a set of deci- and centi-grams comprising that rider, and determining their values by establishing the equation:

$$
\begin{array}{ll}
(\cdot 01) & = (\text{rider}) + \delta_1, \\
(\cdot 02) & = (\text{rider}) + (\cdot 01) + \delta_2, \text{ \&c. up to} \\
(1)_0 & = (0{\cdot}5) + (0{\cdot}2) + (0{\cdot}2)_1 + (0{\cdot}1) \text{ \&c.}
\end{array}
$$

and thus finding out the value of the rider in terms of g. But in practice the rider as a rule does not differ much from ·01g., and this part of the work is not necessary for the sake of the calculation of the errors, the less so as a great value in any of these would simply condemn that piece.

The above method is always used when we test a set of weights with the view of seeing how it falls in with the rest of the sets in the laboratory, which in the aggregate form our set for

general purposes. If the set is meant to be used by itself—if, for instance, we test a set from 50 grms. down to 1 centigr. with the view of using it for our analyses—it is better not to refer to any external standard at all, but to an imaginary unit so chosen that the sum total of the errors becomes nil, *i.e.*, to choose as unit $\frac{1}{100}$ of the actual weight of all the '100 grams' which the 50 gram set represents *in toto*. If one or more of the pieces come out with relatively large errors, the unit is re-adjusted so that it suits only the good pieces, the errors are re-calculated, and the two rejected pieces either replaced by new ones, or re-adjusted. According to the writer's experience, we must be satisfied if the errors of the individual pieces are brought down to values varying from very little to about $\pm 0{\cdot}04$ mgm.

Reduction to the Vacuum.

All weighings executed in air are liable to an obvious correction. Supposing an object occupying V c.c. is balanced in air by p grams of standards occupying v c.c.; if the balance were transferred to a vacuum, the side of the greater V (in our case the object side) would become heavier than the other by $(V-v)\,\delta$ grms. where δ is the weight of one c.c. of air at the time and place. As p is a close approximation to the true weight, the volume of the object in c.c.s can be put down as $p \div S$, that of the standards of course *is* $p \div S_0$, where S and S_0 are the respective specific gravities which practically need not be reduced to water at 4°. The correction to be applied to p is

$$p\delta\left(\frac{1}{S}-\frac{1}{S_0}\right),$$

$$\delta = 0{\cdot}46464\frac{B}{273+t}(\text{mgms.}),$$

where B is the height of the barometer in mm. reduced to 0°C., and t is the temperature; the constant is calculated from Regnault's weight of 1 litre of air of 0° and 760 mm. at London.

For $t=15°$, and $B=760$ mms., $\delta=1{\cdot}22615$, which number, at stations where B is habitually near 760, if the highest precision is not aimed at, may often be taken as holding for air generally.

Standard weights for absolute weighings (in true grams) ought to be adjusted for the vacuum; hence, if the minor weights are of platinum and the larger ones of brass, the brass 1 grm. should appear lighter than its equivalent in platinum decigrams in air. But sets of this order had better be made of one metal.

For a series of relative weighings, the buoyancy of the weight-standards in air may be neglected, because we are at liberty to take as our unit the weight of the 1 grm. piece in air of the average density prevailing during the progress of the experiments. That this unit is strictly speaking variable is of no practical significance.

The vacuum-correction for any single weighing involved in an analysis amounts as a rule to more than we should care to neglect; yet it may be neglected in most cases, because the weight to be determined is only one term of a ratio, whose other term is faulty in the same sense. Suppose we have determined two weights, p_1 and p_2, and we want the correct value x of the ratio of which $p_1 : p_2$ is only an approximation. If the reciprocals of the specific gravity are S_1^{-1} and S_2^{-1} respectively, we have

$$x = \frac{p_1}{p_2}\;\frac{(1+\delta_1 S_1^{-1})}{(1+\delta_2 S_2^{-1})};$$

or as a sufficient approximation

$$x = \frac{p_1}{p_2}\quad(1+\delta_1 S_1^{-1}-\delta_2 S_2^{-1}).$$

And if S_1 does not differ much from S_2 (as δ_1 and δ_2 are always nearly the same) the bracketed factor may come close to unity although neither of the two terms $S^{-1}\delta$ could be neglected if it stood by itself. Here, as everywhere in experimental science, the golden rule is neither to strain at the gnat *nor* to swallow the camel.

Weighing of Gases.

For the weighing of a gas, we have in general three methods.

(1) If the gas to be weighed is a product formed in a reaction between solids or liquids, we may identify its weight with the loss of weight suffered by the reagents during the reaction.

(2) We may collect the gas in a evacuated tared balloon, and weigh it like anything else. In this case it is expedient to tare the flask with another flask of the same displacement and nearly the same weight, so that only a few grams need be put on to establish equilibrium. (Regnault's method). The vacuum-correction is then out of court.

(3) We may measure the gas by volume at a known temperature, t, and pressure, P, and calculate the weight from the volume.

If the gas to be weighed is a product of a reaction carried out quantitatively, one way of measuring it is to construct the apparatus so that the vessel in which the reaction goes on and the gas-measurer have a common atmosphere, and to measure the gas-volume as an increase in the total atmosphere of the apparatus (gas-volumetric method). According to Regnault, 1 lit. of oxygen at 0° and 760 mm. of mercury of 0°C., weighs 1·42932 grams. Hence by an easy computation, based on Avogadro's law, we have for the weight of 1 litre of a given species of gas of the molecular weight M (O = 16)

$$D = 0{\cdot}032089\,\frac{P}{(273+t)} \times \frac{M}{2}\,\text{grams}$$

where P means the dry pressure in mm.

If the gas is moist, the vapour-pressure of steam at $t°$ must be deducted from the observed pressure to find the D of the formula. The constant, strictly speaking, holds only for places where gravity is the same as it is at 45° latitude, and sea-level.

In *Paris*, | *London*, | *Berlin*, | *Glasgow*, it must be multiplied by
1·000333, | 1·000583, | 1·000663, | 1·000956.

Indirect Methods of Mass Measurement.

I. *Physical Methods.*

The nature of these is best explained by a general example. In a given aqueous solution of sulphuric acid, sugar, salt, &c., &c., the specific gravity at $t°$, the refractive index, the power of turning the plane of polarised light (if any), &c., bear each a fixed relation to the

percentage of substance (or the weight of substance per litre) in the solution, which relation is susceptible of translation into a formula $p = f$ (physical property), or a corresponding curve, and by means of either of tabulation. Hence, supposing the function to have been determined by standard experiments, p in a given case can be calculated (virtually or actually) from the value of the respective physical property. In practice we must of course try to establish conditions under which the change in the specific gravity, &c., &c., corresponding to the passing from p to, say, (1·01) p, assumes a sufficiently great value.

The popular method for determining the strength of aqueous oil of vitriol, &c., by means of a hydrometer may be referred to as an example. The customary method of deducing the percentage of sugar in a syrup from the angle through which a column of given length turns the plane of polarised light is another.

II. *Chemical Methods.*

These, being all founded upon our knowledge of the quantitative laws of certain reactions, are methods for the indirect weighing of radicles rather than of substances. Scientifically one might arrange them according to their degree of directness. If we do so, the following two claim precedence before any of the rest.

(1.) *The direct gravimetric method.* An unknown weight of this or that radicle is determined by separating it out exhaustively, by itself or as part of a compound of known composition, and weighing the product either directly on the balance, or perhaps indirectly by gasometric measurement.

(2.) *The method of titration.* An unknown weight of radicle is deduced from the quantity of reagent necessary and sufficient to cause it to undergo a certain definite change of combination; the quantity of reagent being ascertained synthetically, *i.e.* by direct trial.

These two methods we will designate as 'direct' methods in opposition to the following 'indirect' methods.

(3.) *The method of substitution.* Instead of determining a radicle R, we substitute for it an equivalent of some other radicle (or substance) R′; we determine R′ by method I. or II., and from it calculate R. Thus, to determine an unknown weight of free chlorine, x Cl_2 mgms., we substitute x I_2 mgms. by means of the reaction $Cl_2 + 2KIAq = 2KClAq + I_2Aq$, and determine the iodine. In some cases we effect a series of substitutions (R′ for R; R″ for R′; R‴ for R″, &c.), and determine only the ultimate substitute. Thus, to determine x CrO_3, we substitute first $x \times 3Cl$, then for this we substitute $x \times 3I$, and by ascertaining the value $x \times 3I$ we find $x \times CrO_3$.

(4.) *The residue-method.* The body containing the radicle is subjected to a definite chemical change by means of a known (excessive) weight of reagent, and the excess of reagent left is determined.

(5.) *Methods founded upon the numerical difference between formulæ-values*:—We pass at once to examples:—

(*a.*) To analyse a mixture of the compounds AgCl and AgBr, we expose a known weight to the action of dry chlorine until all the AgBr has become AgCl, and determine the decrease of weight involved. From the obvious equation of the reaction, we see that every Br-Cl gram of loss of weight corresponds to Br grams of bromine, or AgBr grams of bromide of silver.

(*b.*) To determine the weight of real sulphuric acid contained in a given quantity of an aqueous acid, we evaporate with a known (excessive) weight of anhydrous carbonate of soda, and weigh the residue (Thorpe). As
$x\,Na_2CO_3 + Na_2CO_3 + H_2SO_4 =$
$CO_2 + H_2O + Na_2SO_4 + xNa_2CO_3$, every $(SO_3 - CO_2)$ grams of increase of weight indicate SO_3 grams of sulphur trioxide.

(*c.*) To analyse a mixture of the sulphates of sodium and lithium; take p grams of the mixture, ppt. all its sulphuric acid with barium chloride, and weigh the barium sulphate.

1 grm. of the sodium salt gives $\frac{BaSO_4}{Na_2SO_4} = s$,

1 grm. of the lithium salt gives $\frac{BaSO_4}{Li_2SO_4} = l$, grms

of barium sulphate. Hence if c grms of pp. were obtained we have (from x grms of sodium sulphate, and y of lithium sulphate)

$$x \times s + y \times l = c$$
$$x + y = p.$$

Whence x and y are easily calculated.

Many other examples might be quoted.

We will now pass to

The Operations involved in quantitative determinations by chemical methods. But first let us say a few words about a necessary preliminary to any quantitative analysis, namely, the preparation of the sample. This problem assumes perhaps its most difficult form if the thing to be analysed is a large mass of imperfectly homogeneous matter, say, a cargo of copper ore. In this case the analysis must of course be preceded by the preparation of a sample, which, although it may amount to only a few pounds, yet can be assumed with a sufficient degree of probability to have the composition of the whole heap. And supposing even a homogeneous sample to have been prepared for the analyst, a mere assay (of the copper in our case) would be of no use unless accompanied by determinations of the moisture in, *a* the ore as it lies, and *b* the small ultimate sample which goes to the balance. An impure specimen of a named chemical species to be rendered fit for the analysis of the species must first be purified, unless we prefer to determine the impurities, and allow for them in the calculation.

In now passing to our subject, we will give the first place to the operations involved in those

I. *Assays by igneous operations*,

which are so extensively employed in practical metallurgy. These, however, are quite a speciality which is almost entirely confined to metallurgical laboratories. Suffice it, therefore, to say that these *assays*, as the name indicates, are, at least by original intention, processes of metal-smelting carried out tentatively on a small scale. The metal is separated out as a regulus either of the metal itself or of some definite arsenide, and in either form is weighed directly on the balance-pan.

II. *Quantitative expulsion of volatile components by exposure of the substance to regulated temperatures.*

Under this heading fall most of our methods for the determination of *water*, given in combination with *non-volatile* residues. Water thus combined, can, as a rule, be driven out with or without the help of a dry atmosphere, by prolonged exposure of the substance to a suitable temperature, and, if other changes are known not to take place, the weight of the water expelled is the loss of weight involved in the drying process.

If the residue, while giving up its water, takes up oxygen or suffers some other change involving change of weight, the water must be expelled in an apparatus so constructed that the steam can be purified (if necessary) and collected without loss by absorption in a weighed U-tube filled with chloride of calcium, or pumice moistened with sulphuric acid, and determined as an increase of weight of the absorption apparatus. We have no means of discriminating experimentally between water present as such (moisture) and water present in chemical combination;[1] nor can we discriminate analytically between the different states of combination which we distinguish in our formulæ. All the analyst can do (after removal of what there may be of palpably free water by mechanical means) is to try, successively, exposure to (1) ordinary 'dry' air; (2) artificially dried air, or a dry vacuum; (3) a graduated series of higher temperatures, such as 100°, 120°, 150°, 200°, in a hot air chamber; (4) a red or perhaps a white heat; and to report the several losses of weight, taking care of course to apply each temperature again and again, until the weight of the residue (or of the calcium chloride tube) has become constant.

From hydrates undecomposable by mere heating, the water must be expelled by suitable reagents. Basic hydrates, like caustic potash, can be dehydrated (quantitatively) by fusion with excess of anhydrous bichromate of potash; many hydrated acids, by evaporation of their solutions with a known excessive weight of oxide of lead, and weighing the dried residue. The writer directs attention to the applicability of tri-sodic phosphate as a weighable form of Na_2O for the latter purpose.

III. *Combustions in glass tubes*, v. ANALYSIS, ORGANIC.

IV. *Carius' general method of ultimate organic analysis*, v. ANALYSIS, ORGANIC.

V. *Gas evolutions.*

We here refer to a class of methods in which the thing to be determined is measured by the weight of a gas evolved in a wet-way reaction of the substance to be analysed. The gas evolved is weighed as loss, or after absorption by a suitable absorbent, or is measured (and thus indirectly weighed) gasometrically (*v. supra*).

VI. *Electrolysis.*

Solutions of many heavy metallic salts, when subjected to a galvanic current under suitable conditions, are fully decomposed, in the sense that all the metal separates out as such on the negative electrode. By properly regulating the strength of the current and the composition of the liquid, it is possible, in many cases, to cause the whole of the metallic pp. to assume the form of a coherent, truly metallic, deposit, so that, if a platinum electrode be used, the metal can be determined as an increase of weight of the latter. The method, however, is not as easy as it is obvious; and is in general use only for two metals, namely copper (Luckow's method), and nickel. Classen[1] has tried, not without success, to extend the method to many other heavy metals; but his processes have failed so far to become popular.

VII. *Gravimetric Precipitation.*

Our heading refers to the very large number of cases in which we determine a component of a solution by separating it out in an insoluble form, and weighing the pp. or converting it into another body and weighing that. With the preliminary separations that may be necessary we can have nothing to do here; we assume that the ppn. has been effected exhaustively, and that the pp. is (in the sense of the method) free from foreign components. In this case the next thing to be done of course is to separate the pp. completely from the mother-liquor. In some cases (for instance in the case of the haloid salts of silver, and of metallic gold ppd. by ferrous salt) this can be done by decantation; but as a rule it is necessary to resort to filtration. For this operation the first requisite is a good funnel, and good filter-paper. The funnel should be a smooth cone of exactly 60° aperture, so that a filter folded in quarto fits it exactly. The best filter-paper for general purposes is that Swedish paper known as Muntkell's; only it filters somewhat slowly, and in many cases, therefore, papers of looser texture are preferable. Filters, which, having been washed with hydrofluoric and hydrochloric acids, leave almost no ash on incineration. In conducting a filtration, the following rules should be observed:

1. Before starting the filtration, allow the pp. to settle completely; then decant off the liquor on to the filter, allowing as little of the pp. as possible to go on to the paper.—2. The same rule holds for the first stages of the washing process; the bulk of the pp. should go on to the filter only after almost all the dissolved matter has been washed away.—3. The wash-liquor should be employed in small instalments, and each instalment be allowed to drain off, before the next one comes on.—4. The washing must be continued until the purity of the last runnings is proved by direct testing. No calculation of the attenuation reached can be relied on implicitly, although it is valuable for preliminary guidance, and may be the only method

[1] According to the current notions on dissociation, a current of (originally dry) air which has passed over a sufficient column of partially dehydrated salt, should take away the free water from a given specimen of *moist* salt of the same kind at the same temperature. Hence an obvious (theoretical) method for recognising free water as such.

[1] Classen: *Quantitative Analyse durch Electrolyse.* [2nd ed. Berlin, 1886.]

available.—5. The filter should fit the funnel closely; it should be smaller than the funnel, and not much larger than is necessary for the convenient accommodation of the pp.

Many pps. run through the paper as soon as the wash-water becomes nearly pure; bisulphide of tin exhibits this property in a marked degree. Addition of some suitable salt (sal-ammoniac, acetate of ammonia, &c.) to the wash-water often helps one over this difficulty.

In the case of slimy or gelatinous pps. (*e.g.* hydroxides of silicon, aluminium, and chromium) Bunsen's method of quick filtration is employed. It consists in this, that the funnel is made to communicate, by its stem, with a vessel in which a partial vacuum of adequate strength is maintained by means of an aspirator (a Sprengel pump wrought with water, or equivalent arrangement). To protect the filter from being torn by the pressure of the atmosphere, its open end is supported by a small cone of platinum foil, resting on the bottom of the funnel. In regard to the operations subsequent to filtration and washing, pps. may be classified as follows:—

A. Such as stand calcination in a platinum or porcelain crucible, and when thus treated assume a definite composition. In this case the general *modus operandi* is as follows: the pp. is dried in the funnel; it is then detached as completely as possible from the paper, and put into the tared crucible. The filter, with adhering particles of pp. is folded up into a narrow strip, and this is rolled up tightly into a parcel, so that the part stained with the pp. is in the core. A platinum wire is then wound round two or three times, and the parcel is kindled in a gas flame and allowed to burn, the surplus wire serving as a handle. After the combustion has gone as far as it will spontaneously, the residual charcoal is burned away by applying the outer portion of the flame of a Bunsen. The ash is dropped into the crucible and calcined along with the pp. In some cases, as for instance in that of alumina, it is better not to detach the pp. from the filter, but simply to fold up the pp. in the filter, and heat the whole in a platinum crucible. Any deposit of charcoal formed on the lid or crucible sides is easily removed by heating the respective part while a shield of platinum foil is stretched over the deposit. The charcoal vanishes almost instantaneously. The weight of the filter-ash must of course be ascertained by a blank experiment, and allowed for. The correction (*cæteris paribus*) is proportional to the superficial area of the filter; *i.e.* ash-weight $= cr^2$, where c is a constant which can be determined once for all.

It is to be observed, however, that even with the same filter-paper, c depends on the nature of the liquid which passed through the filter. It is less for dilute mineral acid, for instance, than for pure water, or salt solutions followed by water.

B. Precipitates which do not stand calcination; but assume a definite composition when dried at a suitable lower temperature, say at 100° or 120°C. Such pps. are collected on filters (previously dried at the respective temperatures) and weighed in the filters. As filter-paper is hygroscopic, the empty filter, and the filter with pp., must be weighed between a couple of closely fitting watch-glasses held together by a suitable clip.

C. Precipitates which demand some supplementary chemical treatment to become fit for the balance. In regard to these it is difficult to make general statements; suffice it to say that certain metallic sulphides assume a definite composition when strongly heated (repeatedly, and until constant in weight) with sulphur in hydrogen gas. The sulphides of copper, manganese, zinc, lead, may be quoted as examples. The resulting definite sulphides are Cu_2S, MnS, ZnS, PbS, respectively.

GAS ANALYSIS.

A large supply of homogeneous gas may be dealt with, analytically, in a variety of ways. With a small gas-sample given for analysis only one mode of treatment could be—or at any rate ever is—thought of. We must collect our gas over mercury, or some other suitable liquid, and learn what we can concerning it by applying physical or chemical reactions, involving changes of gas-volume; we must measure the gas volumes involved as the only practicable mode of defining the respective masses.

Principles of volumetric gasometry. To measure a given quantity of gas means to determine its volume, V, and its pressure, P, at a definite temperature, t. In any *fluid* body of known nature the three quantities conjointly define the mass; yet the method is confined to gases, because in these only is the evidence afforded by the three numbers condensible into *one* numerical statement by mere calculation.

Practical gasometry knows of no pressure greater than two atmospheres (indeed pressures above one atmosphere are exceptional); and of no temperature below 0°C.

Within this range of conditions the law of interdependence between volume, temperature, and pressure, in all gases is in approximate accordance—in the so-called permanent gases it is in perfect accordance—with the equation

$$\frac{VP}{T} = Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where T may be defined as $T = 273 + t$. Q is a constant which depends only on the nature of the gas and its mass, and consequently, in reference to any named species, measures the quantity.

Condensible gases and vapours deviate from the law embodied in eq. (1) to a greater or less extent, but always in this sense that the true relations are expressible by an equation of the form

$$\frac{VP}{T}(1+\epsilon) = Q \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ϵ is an inherently positive number which is a function of T and P, to the effect that, for any given species, ϵ is the less the further the pressure and temperature remove the gas from the state of saturated vapour. Gasometrically speaking ϵ is mainly a function of temperature which runs pretty much like $\epsilon = \text{const}.\frac{1}{T}$; not by any means exactly so, but we are safe in saying that for every gas-species there is a certain temperature T_0 above which this species is, as the phrase goes, a 'perfect

gas, in at least this sense that ϵ is less than the unavoidable error involved in the experimental determination of $PV \div T$ by the customary instruments. In this sense our equation (1) is true for all kinds of gas or vapour without exception.

The constant Q is obviously susceptible of a number of definitions. One definition is to call it the volume which the gas assumes when $T=1°$ and $P=1$ (say 1mm.), or rather the volume which the gas would assume if it were a perfect gas down to $T=1$ or $t=-272°$. To eliminate this fiction, let us view V as a function, not of P and T, but of $\frac{T}{P}$, thus:

$$V = Q\left(\frac{T}{P}\right);$$

and, taking '*disgregation*' as a name for this ratio $T:P$, define Q as that volume which the gas assumes whenever the disgregation is unity through P being equal to T numerically. If, for instance,

	$T=1°$	273°	373°	500°C. &c.
then	$P=1$	273	373	500 mm. &c.

In this manner it is always easy to find for Q a *real* significance. Q, however, has two denominations. Obviously

$$P = Q\frac{T}{V},$$

hence Q may be called the particular pressure which the gas assumes whenever $T=V$; *i.e.* for $T=1°$ and $V=1$ unit; $T=500°$ and $V=500$, &c.

For the purely *comparative* measurement of two or more gas quantities, only one of the three variables need actually be measured.

Assuming the Qs for the gases I, II, III...to be Q' Q'' Q''', &c., we may (1) keep T and P at constant (though perhaps unknown) values and measure the volumes

$$V' \quad V'' \quad V''' \text{ \&c. which are}$$

$$\frac{Q'T}{P} \quad \frac{Q''T}{P} \quad \frac{Q'''T}{P} \text{ \&c.}$$

The constant factor disappears in the ratios. This used to be, at least by intention, *the* method of comparative gasometry.

(2) We may keep T and V constant and measure the pressures P' P'' P''' which are

$$Q'\frac{T}{V} \quad Q''\frac{T}{V} \quad Q'''\frac{T}{V} \text{ \&c.}$$

and consequently again measure the Qs (Regnault's method).

(3) We may allow T and P to vary, but keep their ratio, the *disgregation*, constant, and measure the volumes, *i.e.* substitute for the Qs

$$(Q' \quad Q'' \quad Q'''...) \times \text{a constant } \frac{T}{P}$$

(Doyère's method).

But Q has an important chemical significance. A glance at eq. (1) shows that the specific gravity of a gas, meaning the number of times its weight is greater than that of the same volume of some standard gas of the same disgregation, is independent of T and P. As stated by Avogadro, and since proved by numerous experiments, we have for any set of gas-species

$$s' : s'' : s''' ... = M' : M'' : M''' ......$$

or quite generally

$$S = \text{const. } M \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where M is the mol. weight.

Hence supposing, at a given disgregation unit volume of standard gas weighs R units, then unit vol. of another gas of the mol. w., M weighs $R\frac{M}{M_0}$, where M_0 refers to the standard gas. Hence unit-volume of any gas, if measured at that disgregation, contains $\frac{R}{M_0} \times M$ units of weight of its substance; hence equal volumes of any two gases, if measured at the same disgregation, contain the same number of molecules, where 'molecule' *may* have the usual meaning given to this term. Hence our constant Q, or any of its substitutes as given above under (1) (2) and (3), in a relative sense counts the molecules of the respective gas.

Eq. (1) tells us nothing about the relation between the volume V of a gas-mixture, and the volumes v' v'' v'''...of its components; but we know, by direct experience, that $V = v' + v'' + v'''$...;[1] hence Avogadro's law holds for mixed as well as for homogeneous gases; and, independently of it, we have

$$q' + q'' + q'''... = Q \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and at any constant value of $V \div T$

$$p' + p'' + p'''... = P \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(where the small letters refer to the components and the large ones to the mixture). And so quite generally

$q : Q = v : V = p : P =$ (number of mols. in the component): (number of mols. in the mixture) . . . . (6)

Hence our customary mode of stating the composition of a gas-mixture is susceptible of three readings. Instead of saying (1) 100 volumes of air contain 21 vol. of oxygen and 79 of nitrogen; we may say (2) the partial pressure of the oxygen is 21 p.c. and that of the nitrogen 79 p.c. of the total pressure of the air; or (3) every $n \times 100$ mols. of air contain $n \times 21$ mols. of oxygen and $n \times 79$ of nitrogen.

In the more easily condensible gases, the number ϵ (which might be called the measure of gaseous imperfection) assumes appreciable values at the ordinary temperature; yet in the ordinary practice of gas analysis even these gases are customarily being measured at, or near, the temperature of the laboratory. To give an idea of the possible value of the error thus neglected we will take up the case of carbonic acid, which, of ordinarily occurring gases, is perhaps the most imperfect.

According to Amagat, carbonic acid, from 0°C. upwards, expands at a greater rate than air, up to about 200°, whence onward it behaves like a perfect gas in reference to expansion caused by changes of temperature or pressure. At 760° mm. its expansion from 0° to 200° is in the ratio[2] of 1 : 1·74065. Hence supposing we find for a quantity of carbonic acid $v = v_0$, for $T = 273$ and $P = 760$, we have for the constant Q:—

(1) By the ordinary routine mode of calculation, *i.e.* by eq. (1); $Q' = \frac{v_0 \times 760}{273}$;

[1] It is worth while to note that this all-important proposition has never been looked into in the Regnault-fashion.

[2] Calculated by the writer from the coefficients of expansion stated by Amagat for 50°, 100°, 180°, and 200°.

(2) For the true Q;

$$Q_0 = \frac{v_0 \times 1{\cdot}74065 \times 760}{273}.$$

Whence $Q_0 = 1{\cdot}0046\ Q'$; or in the sense of our equation (2), for $T = 273$ and $P = 760$ mm.

$$\Delta Q_0 = \frac{v_0 \times 760}{273}(1+\epsilon);\ \text{and}\ \epsilon = 0{\cdot}0016. \quad (7)$$

This number, or say 0·005, might perhaps be put down as the maximum value which ϵ may assume in the customary mode of measuring gases proper, were it not for the following consideration. As a rule the gas to be measured is contaminated with vapour of water, and it is the Q of the *dry* gas that is wanted. One mode of obtaining it is to remove the water by chemical absorbents and to measure the dry gas; but this is a tedious process; hence we prefer, in practice, to saturate the gas completely with water, to measure it in this condition, and, before calculating by eq. (1), to correct the observed pressure by deducting the maximum steam-pressure at the respective temperature, as determined by Magnus and by Regnault for the vacuum, assuming the corrected value $P_0 = P - \pi$ to represent the pressure which the gas would exhibit at the same vol. and temperature if it were dry. As shown by Regnault, this is not quite exactly the case, yet if π is small, *i.e.* if the *temperature* is *low*, the error may be neglected. A low temperature, it is true, means a relatively great ϵ, but π certainly, and the error in π probably, increases (with t) much faster than ϵ decreases.

Both the authorities named give their πs in terms of the pressure of a column of mercury of 0°C. whose height equals 1 mm. Hence to be able to use their numbers directly we must provide our eudiometers and barometer with true mm.-scales. And we ought to reduce all mercury columns (measured as pressures) to 0°C. This, however, is necessary only in the case of absolute measurements, *i.e.* if we measure a gas as a step towards calculating its weight; for relative measurements we may choose our units for V, T, and P, at pleasure,[1] hence the absolute magnitude of our 'mm.' is of no consequence. Nor is it necessary to reduce the π to what our mm. is at the respective temperature, because the correction is practically irrelevant.

Gases like hydrochloric acid, ammonia, sulphur dioxide, &c., must be measured dry—for an obvious reason.

Gas-Analysis. (a) *Proximate.* For the proximate analysis of a gas-mixture we have only one direct method. After having measured off a convenient sample, we withdraw the several components (singly or in groups), by the successive application of appropriate chemical absorbents, as pressureless solids or liquids, and, after each absorption, we measure the gas-residue left. Supposing the sample measures V units at T and P, and the same, minus component I, measures V′ units at T′ and P′; we have for the sample $Q = \frac{VP}{T}$, for the residue $Q' = \frac{V'P'}{T'}$; hence for the percentage of I; $x = \frac{Q - Q_1}{Q} \times 100$.

To show the possibilities of the method, we enumerate the most important reagents and state the powers of each as an absorbent.

(1) *Water* (as such or as $Na_2SO_4 10H_2O$) absorbs HCl, HBr, HI, very promptly.

(2) *Solid* DRY *caustic potash* absorbs water very completely; acid gases generally more or less slowly.

(3) *Solid* MOIST *caustic potash* absorbs all acid gases (CO_2, SO_2, H_2S, HCl, &c.) very readily.

(4) *Caustic potash solution* acts like (3) and (1).

(5) *Dilute sulphuric acid* absorbs all alkaline gases (NH_3, CH_3NH_2 &c.); besides acting as water.

(6) *Oil of vitriol* ($H_2SO_4 + \frac{1}{12}H_2O$) absorbs (*a*) water, alcohol, ether, methyl-oxide, very readily; (*b*) propylene and higher homologues, with a fair degree of promptitude. C_2H_4 is absorbed only on long-continued shaking (Berthelot).

(7) *Sulphuric anhydride* in H_2SO_4 absorbs C_2H_4 in addition to the gases named in (6).

(8) *Bromine* (over water in diffused daylight) acts pretty much like (7); the excess of Br vapours left is removed by means of KHOAq.

(9) *Pyrogallic acid in caustic potash ley* absorbs oxygen abundantly and promptly (Liebig), besides acting like (4).

(10) *Cuprous chloride in hydrochloric acid* absorbs oxygen; also CO, C_2H_2, C_3H_4 (Bertholet).—Spoils the mercury.

(11) *Same reagent in aqueous ammonia* acts like (10), and besides absorbs certain other gases, *e.g.* all the olefines (Berthelot).

(12) *Ferrous sulphate in concentrated solution* absorbs nitric oxide; but hardly in the chemical sense, as the compound has a measurable dissociation-pressure.[1]

(13) *Binoxide of manganese*, as compressed powder, is used by Bunsen for absorbing H_2S and SO_2.—Solution of CrO_3 or of $KMnO_4$ acts similarly and more promptly.

(14) *Chromous sulphate in NH_3 and NH_4Cl solution* absorbs O, NO, C_2H_2, C_3H_4, but does not act on CO, C_2H_4, or C_3H_6 (Berthelot).

That all gas mixtures cannot be analysed by means of these 14 reagents is obvious. Unfortunately they are all group-reagents, and a group when once absorbed is not susceptible (practically) of further gasometric analysis. One or other of the absorbed components may be determinable otherwise—thus for instance H_2S (absorbed in KHO) by titration with iodine—but these are rare exceptions. For the analysis of a gas-mixture which, with regard to chemical absorbents, behaves as a whole, only two methods are at our disposal; one is to determine the ultimate composition of the gas (if possible), and from the results to try and arrive at the proximate composition; the other is to examine the gas by means of physical absorbents. But to obtain definite results with these we must follow the lead of Bunsen, and both contrive their application and interpret the results, in the light of the laws of gas-absorption.

Analysis by physical absorbents.

Imagine v volumes of a mixture of the unitary gases I., II., III., . . . to be shut up

[1] *I.e.* we may, if we choose, measure our *t*s with a Fahrenheit thermometer and take T as being $T = 459{\cdot}4 + t$ (in F. degrees).

[1] NO is absorbable also by the conjoint action of O and KHO solution, as KNO_2 and KNO_3.

in a close vessel over h volumes of water or alcohol, an impervious diaphragm separating the two. As soon as the diaphragm is removed, the gas and liquid exchange molecules, and this goes on for ever; but if a constant temperature t is maintained, a point is reached, sooner or later, at which the changes of composition, exactly compensate each other, so that matters are the same as if the exchange had come to a stop. This point of dynamical equilibrium is reached almost instantaneously on violent shaking. The final result is that the gas-space v is saturated with the vapour of the liquid, while a quantity q of each of the components of the gas is held in solution by the h volumes of liquid. This quantity q *at a given temperature* is in (more or less exact) accordance with the equation—

$$q = h\beta\pi \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where π means the partial pressure of the respective component in the residue, and β is a constant, which may be defined as being the value which q assumes when $h=1$ and $\pi = 1$ mm. q and β are, of course, of the same denomination; if q means mgms., β means mgms. likewise. But we will assume q to be measured by volume at 0° C. (or T = 273° C.) and P = 1 mm., and on the basis of this assumption (with Bunsen) call β the 'co-efficient of absorption.'

Our equation has been tested experimentally only with water and, in a more limited sense, alcohol, as a solvent; and in reference to either, it may be assumed to hold, at pressures up to about 1 atm., and temperatures from 0° to about 30° C., for all gases which, under the circumstances, do not act chemically on, or dissolve very abundantly in, the respective liquid. With a given gas-species, β, in general, increases when the temperature falls, or when alcohol is substituted for water. It has, in general, different values for different species of gas. Hence we at once see our way towards distinguishing a unitary gas from a mixture. Take, for instance, the case of marsh-gas CH_4 as against a mixture of equal volumes of H_2 and $C_2H_6 = CH_4$ per 1 volume. With alcohol as an absorbent, the β of C_2H_6 is far greater than that for H_2. Hence, if the mixture be dissolved partially by alcohol, the residue will contain less carbon per unit volume than $\frac{1}{2}C_2$; and similarly in similar cases.

The relation between the composition of the mixture operated upon and that of the unabsorbed residue is easily formulated. Let m', m'', &c., stand for the quantities of the several components present in unit volume of the original gas, and let n', n'', &c., have a similar meaning in reference to the residue; let P stand for the (dry) pressure of the original gas, and p for that of the residue, then we have for any one of the components $q = h\beta(pn)$; and for the unabsorbed part of that component

$$r = (np)v\frac{273}{273+t} = (np)''v_0'',$$

and $q + r = pn(v_0 + \beta h)$; but $q + r = \text{P}mv_0$, hence $\text{P}mv_0 = pn(v_0 + \beta h)$, which enables us to calculate the 'n' of a named component from its 'm.' For further developments we refer to Dittmar's 'Exercises in Quantitative Analysis,' section on gas analysis (Glasgow, W. Hodge & Co.). Without mathematics it is clear that the quantity, λ, of total gas absorbed, reduced to $p=1$ and $h=1$, is

$$\lambda = \frac{v_0(\text{P}-p)}{hp}.$$

In the case of a unitary species λ is the *co-efficient of absorption*, and is consequently constant, while, in the case of a mixture it varies (in general) with $h{:}v$, *i.e.* with varying quantities of water for the same quantity of gas started with. Hence an obvious second method for testing a gas for chemical oneness.

Of general methods of gas analysis, only one remains to be considered. We refer to the

Method of Combustion.—A method of ultimate analysis which presumes that the gas to be analysed is in, or by addition of hydrogen or of oxygen or of either plus fulminating gas,[1] can be brought into, such a condition, that the mixture, when fired with an electric spark is resolved entirely into (in general) carbonic acid, nitrogen, and water, and excess of either hydrogen or oxygen as the case may be. The method consists in this that a measured volume of the given gas is exploded, and the gas quantities involved are measured as far as necessary to enable one to calculate the *elementary* composition of the gas under operation, the results being regarded customarily in volumes (reduced to some tacitly assumed constant disgregation) of the respective elementary substances. For uniformity's sake this system is extended even to the carbon, one volume of carbon being used as a phrase for the quantity of carbon contained in two volumes of carbonic anhydride. This mode of reporting comes to the same as stating the quantities of hydrogen, oxygen, &c., as multiples of the molecular weights H_2, O_2, N_2, and of the double atom C_2 of carbon. In the sequel we sometimes use H_2, O_2, N_2, CO_2, CO, as symbols for '1 volume.' When in a calculation we have to refer to a certain (reduced) volume of carbonic acid we designate it by the letter K; in a similar sense S refers to oxygen; W to water vapour; $\mathfrak{N}$ to nitrogen ('N' is reserved for the atom); C to contraction. The following examples explain the method:

I. The gas is a mixture of hydrogen and hydrocarbons; *i.e.* 1 vol. $= \alpha C_2, \beta H_2$. We determine the following gas-quantities:

(0) The volume of the sample, as . V
(1) " " plus added oxygen, as . . . V_1

And after firing

(2) The volume of the total product measured cold, as . . V_2
(3) The volume of the residue left after removal of the carbonic anhydride, as . . . . . V_3

The quantity of carbonic anhydride produced in the combustion is '$K' = V_2 - V_3$, whence $\alpha = \frac{1}{2}\frac{V_2 - V_3}{V}$.

The hydrogen is calculated from the '*contraction*,' meaning the difference '$C' = V_1 - V_2$, thus: $V_1 = V + S$, where S stands for the added oxygen.

$V_2 = K +$ oxygen left unburnt, which is $S - K - x$,

[1] The mixture $H_2 + \frac{1}{2}O_2$ obtained in the electrolysis of water.

where x means the oxygen which converted the hydrogen into water. Hence $c = v_1 - v_3 = v + s - [\kappa + (s - \kappa - x)]$ or $c = v + x$; hence $x = c - v$, and $\beta = \frac{2(c-v)}{v}$.

The sum $\alpha + \beta$ is, of course, always greater than unity unless $\alpha = 0$.

We will assume now

II. That the gas contains (in the v units taken for analysis) z volumes of free oxygen and y volumes of free nitrogen beside v_0 of hydrocarbons; both z and y being unknown. Here we at once see that the measurements of v_1, v_2, v_3, do not enable us to calculate z or y. But we cannot even calculate the volume x of oxygen which combined with the hydrogen in the combustion; because from case I. we see that $x = c - v_0$, and v_0 is unknown. Nor does a direct determination of the oxygen-residue s_r in v_3 help us, because s_r is a function of c, independent of x and z. We have, in fact:—

$$s_r = z + s - x - \kappa;$$
$$c = v - (z + y) + x;$$
$$s_r + c = s - \kappa + v - y;$$

and
$$s_r = -c + s - \kappa + v - y.$$

The determination could only confirm this calculation. If z is known to be $= 0$, or z and y conjointly are known to be so much *air*, the problem becomes easy of solution.

III. The gas is $\alpha C_2.\beta H_2.\gamma O_2.\delta N_2 = 1$ volume; states of combination unknown. If we add to the values (for v of substance) of κ and c that of the nitrogen in the ultimate residue (let its quantity be $= \Omega$) we have α and δ at once. But, (even supposing we did not care for γ), to determine β we must measure the quantity, w, of steam produced in the combustion. From w we have $\beta = \frac{1}{v} w$; and from this, and the contraction c, we can calculate γ thus; let s_0 denote the quantity of oxygen which, conjointly with the oxygen in the substance, is just sufficient to burn the substance into CO_2, H_2O, and N_2, and let s_r be the surplus added, so that $s_r + s_0 = s$; we have

$$v_1 = v + s_0 + s_r$$
$$v_2 = \Omega + \kappa + s_r$$
$$c = v + s_0 - \Omega - \kappa;$$

or,
$$v_1 - v_3 = v + s_0 - \Omega.$$

Now, it was obviously the oxygen sum $s_0 + v\gamma$ which produced the H_2O and CO_2; hence,

$$s_0 + v\gamma = \kappa + \tfrac{1}{2}w;$$
$$\therefore \quad \gamma = \frac{1}{v}(\kappa + \tfrac{1}{2}w - s_0).$$

Whenever, in a gas of unknown constitution, oxygen *may* be present, the determination of w becomes indispensable, because without it the water possibly present in a gas would escape us altogether; we could not, for instance, discriminate between ethylene and oxide of methyl.

The case which we have just been discussing includes that of the analysis of any gas $\gamma O_2.\delta N_2$ which is combustible by means of hydrogen. Because the added hydrogen, for calculating purposes, may be included in the 'v' of our formulæ, to be ultimately allowed for. In practice, however, the variety of proximate compositions included in the formula $\gamma O_2.\delta N_2$ is very small, so that, in the case of such a gas, we had better at once calculate the proximate components (N_2, N_2O, O_3 &c.) directly from the data of the combustion.

IV. Let us now see how far the method of combustion goes as an *indirect* method of proximate analysis. Let us assume that we have to deal with a gas of the nature pre-supposed in case III., and that the quantities, κ, c, w, Ω, have been determined, and none of them found $= 0$. We also assume that we know the formulæ of all the several species I., II., ..., which can possibly be present. To find the quantities of these contained in unit-quantity of the given gas (x' for I.; x'' for II. .....) we might begin by calculating the *elementary* composition of our gas, *i.e.* the coefficients in the average formula $\alpha C_2.\beta H_2.\gamma O_2.\delta N_2 = 1$ vol., and then express these algebraically in terms of the special values α', α'' ......, β', β''......, &c., appertaining to the components I., II......., &c., thus,

$$\alpha = \alpha' x' + \alpha'' x'' + \alpha''' x''', \text{ \&c.} \qquad \text{I.}$$
$$\beta = \beta' x' + \beta'' x'' + \beta''' x''', \text{ \&c.} \qquad \text{II.}$$
$$\gamma = \gamma' x' + \gamma'' x'' + \gamma''' x''', \text{ \&c.} \qquad \text{III.}$$
$$\delta = \delta' x' + \delta'' x'' + \delta''' x''', \text{ \&c.} \qquad \text{IV.}$$
$$1 = x' + x'' + x''', \text{ \&c.} \qquad \text{V.}$$

In practice, of course, we need not calculate α, β, &c., but may at once form equations between $\frac{1}{v}\kappa = k$; $\frac{1}{v}c = c$; $\frac{1}{v}\Omega = n$, &c., and the special values $k'k''$..., $c'c''$..., $n'n''$..., thus—

$$k = k'x' + k''x'', \text{ \&c.} \qquad \text{I.}a.$$
$$c = c'x' + c''x'', \text{ \&c.} \qquad \text{II.}a.$$
$$w = w'x' + w''x'', \text{ \&c.} \qquad \text{III.}a.$$
$$n = n'x' + n''x'', \text{ \&c.} \qquad \text{IV.}a.$$
$$1 = x' + x'', \text{ \&c.} \qquad \text{V.}a.$$

and solve *these* equations; but the former set shows more clearly how far the method goes as a method of proximate analysis.

From either set we at once see that if the number of potential components does not exceed *five*, we can in general calculate the quantity of each in unit quantity of gas, *i.e.* $x' x''...x^v$. *In general* we say, because obviously if one or more of the co-efficients α, β...is $= 0$, so many equations collapse; in the case, for instance, of $\gamma = 0$ and $\delta = 0$, only three equations are left. And (to adhere to the example) if it should happen that all the values of β are the same function of the respective values α, then equation II., or, if you prefer it, equation I., is lost, and only the case of two components is susceptible of a solution. A similar result occurs if all the components should happen to contain the same number of hydrogen-atoms (or the same number of carbon-atoms) per molecule. Supposing, for instance, all the components were of the general formula C_xH_6 then β would by necessity be $= 3$, and equation II. would be resolved into $3 = 3x' + 3x'' + 3x'''$... which is a mere repetition of equation V. And similarly, if all the components were di-carbon gases, equation I. would become useless.

The general rule is, first of all to find out how many of the quantities k, c, n, w... *in addition to our knowledge of the constitution of the gas*, we should need to calculate the co-efficients α, β... of the average formula. Supposing 4, 3, 2 suffice, then (in general) 3, 2, 1, (but not *any* 3, 2, 1), equations of the second set, taken along with equation V..., will suffice to find the un-

known quantities x', x''... sought, provided their number does not exceed 4, 3, 2.

For examples see the writer's *Tables to facilitate chemical calculations* (Williams & Norgate).

The following table gives the values of c, k, s_0, w for several gases.

I.—*Combustible by Oxygen.*

	c	k	s_0	w	n
Hydrogen, H_2	1·5	0	0·5	1·	0·
Carbonic oxide, CO . .	0·5	1	0·5	0·	0·
Methyl-aldehyde, CH_2O	1·	1	1·	1·	0·
Ammonia, NH_3 . . .	1·25	0	0·75	1·5	0·5
Methylamine, CH_5N .	1·75	1	2·25	2·5	0·5
Cyanogen, N_2C_2 . . .	0·	2	2·	0·	1·
Hydrocyanic acid, NCH	0·75	1	1·25	0·5	0·5
Marsh gas, CH_4 . . .	2·	1	2·	2·	0·
Acetylene, C_2H_2 . . .	1·5	2	2·5	1·	0·
Ethylene, C_2H_4 . . .	2·	2	3·	2·	0·
Ethane, C_2H_6	2·5	2	3·5	3·	0·
Propylene, C_3H_6 . . .	2·5	3	4·5	3·	0·
Propane, C_3H_8 . . .	3·	3	5·	4·	0·
Oxide of methyl, C_2H_6O,	2·	2	3·	3·	0·
Benzene, C_6H_6 . . .	2·5	6	7·5	3·	0·
1 vol. = $C_\alpha H_\beta$	$1+\frac{\beta}{4}$	α	$\alpha+\frac{\beta}{4}$	$0·5\beta$	0·

II.—*Combustible by Hydrogen.**

	c	h	w	n
Nitrous oxide, N_2O . .	1·	1·	1·	1·
Nitric oxide, NO† . . .	1·5	1·	1·	0·5

The Practice of Gas Analysis.

In this section we take cognisance only of the chemical methods, and in regard to these confine ourselves in the main to those apparatuses in which mercury serves as a trapping fluid.

Taking ordinary laboratory appliances for granted, all that gas analysis demands of special apparatus is: a barometer, a pneumatic trough with transparent sides, and a series of glass tubes, closed at one end and open at the other, and provided, virtually, with two scales, of which one divides the gas capacity, and the other the axis, into units of sufficient smallness. One or more of these tubes must be provided near the closed end with a couple of fused-in platinum wires so that a combustible gas-mixture in it may be exploded by means of an electric spark. The possibility of obtaining exact results by means of these simple contrivances is proved by the fact that all the great gasometric work of Cavendish and Gay-Lussac, which laid the foundations for our present chemistry, was done with apparatus like those referred to, or even with apparatus of a lower order of complexity. Of course to obtain exact results we must be alive to all the numerous sources of error involved, and eliminate them as far as possible experimentally or otherwise. It is one of the merits of Bunsen to have done this for us, and to have thus brought the old method of gas analysis into a form which, on the score of precision at least, leaves nothing to be desired.

Bunsen's Apparatus and Methods. The first requisite of exact gas analysis, Bunsen says, is a special room in which the temperature is subject to only slight, and to no sudden, variations. The ideal gas-room forms part of a substantial building; it is not warmed artificially nor is it contiguous to any other room thus heated; and its windows face the North, to keep out the sun. In such a room the temperature during a working-day remains constant as a rule to within 1°C. although the variations of temperature of the outside air may amount to as much as 12°C. A characteristic of Bunsen's method is that the chemical treatment of a gas is effected in the tube in which it has been measured; but he uses two kinds of tubes, one for the absorptions, the other (eudiometers) for the combustions. Both are about 20 mm. wide (inside measurement; in narrower tubes the capillarity assumes measurable values) and 2 mm. or so strong in the body, which strength suffices even for the eudiometers. The absorption tubes are about 250 mm. long, and are provided with spouts, so that a gas contained in one can be transferred to another tube by laying down the absorption tube in the trough. In the case of the eudiometers a length of 500–600 mm. suffices for all ordinary purposes. The platinum wires are fused in somewhere near the closed end, and are bent so that the two ends stand opposite each other at a distance of about 2 mm. Every gas tube is provided with an etched-in millimetre-scale, and the gas-volumes corresponding to the several marks are determined by calibration, so that each tube is a laboratory, a volumeter, and a manometer, in one. The scale is figured from the closed end downwards. To calibrate a tube it is fixed, open end upwards, in a vertical position; successive, exactly equal, quantities of mercury are introduced, each corresponding to some 20 mm. of scale, and after each such addition the exact position of the top of the meniscus in reference to the scale is observed by means of a horizontal telescope standing at a distance of 1–2 metres, and the readings are taken down, care being taken, before each reading, to remove any air-bells that may be imprisoned between the mercury and the sides of the tube, by means of a long stick of whalebone. The measuring off of the standard volume of mercury is effected by means of a short stout test-tube, ground exactly flat at its lipless rim, and provided with a lid of ground plate-glass. It is filled from a pipette-like reservoir provided with a long narrow outlet tube and a stop-cock at the top end of this tube. If care be taken so to operate that the mercury, while it fills the measure, forms one continuous mass, the formation of air-bells is easily avoided. The measure, while being filled, is held in a wooden clip (not directly in the hand, which would cause the mercury to expand) while the lid is slung to the thumb of the same hand. The measure is filled to overflowing, the excess of mercury is removed by putting on the lid, and the mercury is poured into the tube.

The mercury-measure is assumed to hold

* h = hydrogen necessary for combustion.

† Nitric oxide cannot be burned with H_2 alone; it requires addition of a certain proportion of N_2O; and even then the combustion is irregular (Bunsen, *Gas. Meth.* 2nd Ed. pp. 95, 96).

'v' volumes of mercury, v being so chosen that, for differences of capacity at least, the numerical value of the volume corresponds as nearly as possible with the respective scale readings, so that, for small differences, every 1 mm. of difference of level can be assumed to correspond to unit-volume (*i.e.* to Δ V = 1). Supposing after addition of k measures full of mercury the meniscus stands at R mm., the volume of the body of quicksilver now in the tube is kv units by definition; but the gas-volume corresponding to R is greater than kv, by the volume x of the |><|-shaped space between the meniscus as it is when the gas is being measured, and the meniscus as it was in the calibration. To determine x, we pour some corrosive sublimate solution on the meniscus (after having read off the number R in calibration) which causes the meniscus to flatten out into a plane, and we read the position of this plane which stands say at R–δ mm. Counting from some horizontal reference-plane 00 upwards, the volume of the mercury and the total space from 00 to the horizontal plane through R are constant. The volume $\frac{1}{2}x$ has become visible as a cylinder of the height δ millimetres, and consequently of the capacity of δ 'units.' Hence the gas volume corresponding to point R is $kv + 2\delta$. From the values $kv + 2\delta$, and the corresponding readings R′ R″ R‴ &c., it is easy (though tedious) to calculate a calibration table which gives all the gas-volumes from mm. to mm. directly. In reading off with a good telescope one soon learns to divide every individual degree into tenths by the eye; the (ΔV)s corresponding to them are found by interpolation from the tabular entries. Should the tube be used for measuring over water, we remove the meniscus-correction by subtracting 2δ from the registered volume, and thus obtain as good an approximation to the gas-volume over water as is called for in such a case.

During the course of the calibration the temperature of the mercury must be kept as nearly as possible constant, or else the values recorded for the lower marks may be very appreciably incorrect. It is well to record the mean temperature t_0 during the period of calibration, and to determine the weight in grams of a measure-full (v 'volumes') of mercury at $t°$, in order to be prepared for reductions of gas-volume to gas-weight. One gram of mercury at 0°C. occupies 0·07355 c.c. (log. $\bar{2}$·866589), and the volume at t°C. is 0·07355 (1 + 0·0001814 t) c.c.

To prepare a eudiometer for receiving a gas we first make it rigorously clean, and next, if the gas is meant to be measured 'moist,' attach a small drop of water to the closed end, which during the operation of filling with mercury gets flattened out and spread over the inside, and so offers a large surface to the gas. The mercury is introduced through a long funnel-tube (provided with a stop-cock at the bottom of the funnel) which goes to the bottom of the eudiometer. By means of this arrangement it is easy, after the introduction of the first thimble-full of metal, to let the mercury in eudiometer and funnel form one unbroken mass, and thus to avoid formation of air-bells at the sides of the tube.[1]

Assuming the gas to have been introduced, and the tube to have been fixed in a vertical position, we begin by preparing for the reading of the level of the trough by inserting a paper screen, provided with a ◯ shaped perforation, between the mercury and the front (glass) wall of the trough, which gives a fairly distinct image of the line of intersection between scale and trough-level plane; we then suspend the thermometer somewhere close to the tube and next leave the room for a time to allow the gas to assume the temperature of the air. On returning we read off:

1. The position R of the meniscus in the tube.
2. The level of the mercury in the trough, R_0.
3. The temperature, $t°$.
4. The barometer; let its height be = B mm.

This reading comes last because the barometer requires to be tapped before being read and this cannot be done from a distance.

In the vast majority of cases the temperatures $t't''t'''$... for the several gases to be compared do not differ much from their mean; hence, even if they differ considerably from the temperature which prevailed in the calibration, the value furnished by the calibration table for R can be put down as the correct relative volume of the gas measured; and the pressure of any mercury-column measured may be identified with its nominal height in mms. as read. Hence we have for the pressure of the dry gas at the observed volume $P = B + R - (R_0 + \pi)$ where π is the maximum pressure of steam at $t°$, and for the gas-quantity (the volume reduced to unit disgregation) $v_0 = \dfrac{v\,P}{273 + t}$ (see theoretical part).

Bunsen prefers reducing to 0°C. and 1000 mm. pressure by the formula

$$v_0 = \frac{v\,P}{1000(1 + 0{\cdot}003665t)}$$

which, if a table of the logarithms of all the values $(1 + \alpha\,t)$ is at hand, is as short a method as the one recommended by us.

Corrections of tube-capacities and mercury-heights for variations of temperature occur only in the rare case when one of the gases concerned in the analysis was measured at an artificially established high temperature t. In this case the value V furnished by the calibration table for the reading R must be corrected thus:—

(True capacity down to R) = $V[1 + \lambda(t - t_0)]$

where λ stands for the coefficient of the cubical expansion of glass, and may be put down at $27{\cdot}6 \times 10^{-6}$. And for the observed height h of a mercury column measured at a high temperature t we must substitute the height h_0 of the equivalent column of mercury of t_0 degrees. t_0 stands in both cases for the average temperature that prevailed during the determinations made in the ordinary manner. Obviously $h_0 = \dfrac{h(1 + k\,t_0)}{1 + k\,t}$ and with sufficient exactitude.

$$h_0 = h\,[1 - k\,(t - t_0)]$$

[1] In regard to the collection and preservation of gas samples, and the mode of introducing a sample into the eudiometer, we refer to Bunsen's *Gasometrische Methoden*, second edition, Braunschweig, 1877. The first edition, 1857, was translated into English by Roscoe, and published by Walton and Maberley, London.

$k = \cdot 00018$.—Strictly speaking the nominal value L of a piece of millimetre-scale as measured at t should be corrected thus:

$$(\text{True length at } t) = L(1 + (t - t_0)9{\cdot}2 \times 10^{-6}).$$

(It is easier to remember that 1000 mm. expand by 0·92 mm. per 100° of increase of temperature.) But our work must be very exact to be worth this correction. It is more relevant to state that whenever we wish to make use of Regnault's determinations of absolute gas-densities we must measure by his unit of (temperature and) pressure, and consequently reduce our mercury-columns to true mm. of mercury of 0°C. Regnault's densities D, on the other hand, ought to be reduced to the gravity of the place of observation; this correction, however, may as a rule be neglected.

For the execution of an *absorption* the most obvious method is to shake the gas with the respective reagent in the liquid form, and to measure the gas-residue as it stands over the layer of liquid reagent. But this method is in general attended with a number of obvious grave errors, and, besides, does not readily adapt itself to the successive application of different reagents. To overcome these difficulties Bunsen, as a general rule, uses all the absorbents in the form of solid or semi-solid balls, fixed each to the end of a platinum wire. Caustic potash, chloride of calcium, &c., are cast in a bullet-mould around the coiled-up end of the wire. To bring sulphuric acid, alkaline pyrogallate-solution, and other intrinsically liquid reagents into a *quasi*-solid form, a ball of some suitable porous material—battery charcoal for vitriol; papier-maché for pyrogallate, &c.—is fixed to the end of the wire and the ball is then soaked in the respective liquid. In this manner it is quite possible to accomplish an absorption even with oil of vitriol, without soiling the tube or the mercury to an inconvenient degree. Reagent vapours left after an absorption, or foreign vapours produced by the reagent—*e.g.* the SO_3 and SO_2 which are always left after an absorption of olefines by fuming vitriol—must of course be removed by suitable reagents (SO_3 and SO_2 by a soft potash ball) before the residue is measured. As small remnants of, for instance, KHO, remain unavoidably in the tube, the residues must in general be measured dry, because the pressure of water in the presence of moist KHO is incalculable.

The weak point in Bunsen's method is that it is tedious, and that it does not enable one to see the end of an absorption otherwise than by the repetition of the process with a fresh reagent ball. Bunsen himself has indeed come to effect carbonic acid absorption, by shaking the gas with solution of caustic soda, and measuring the gas-residue over the layer of reagent. To be able to correct for the pressure of this layer and for the vapour-pressure of the reagent, he employs it in the form of a standardised solution containing exactly 7 p.c. of NaOH, which has a practically constant specific gravity. He has also determined the course of the pressure-curve by standard experiments; the results are embodied in a table appended to his *Gasometrische Methoden*, second edition.

In this connection we must refer to an ingenious method devised by Russell (*C. J.* [2] 6). He introduces the reagents as solutions by means of a graduated syringe; and after they have done their work, removes them by means of a ball of cotton-wool, previously rendered air-free by kneading it under mercury. To remove what adheres to the tube and mercury he rinses the inside with some injected water and removes this by a fresh cotton-wool plug.

In the analysis of a gas by combustion a necessary preliminary step is to remove (and determine) what there may be of SO_2, CO_2, NH_3, and similar gases, by suitable absorbents. Part of the residue is transferred to the eudiometer and measured. Let its volume (reduced to, say, unit disgregation) be equal to v units. The necessary quantity of oxygen or hydrogen is now added and its quantity is determined by measuring the mixture (let its red. volume be v'). The mixture is now rendered explosive, if necessary, by adding the requisite proportion of fulminating gas, the whole is well mixed and prepared for explosion by pressing the open end of the eudiometer firmly against an india-rubber pad lying on the bottom of the trough. The upper surface of the pad must have been rendered air-free by rubbing it over with a few drops of corrosive sublimate and mercury. After these preliminaries the combustion is effected by passing an electric spark through the mixture. After the combustion, the eudiometer is carefully lifted from its cushion, so that the mercury enters slowly and without drawing in air. The gas, after having been allowed to cool down to the temperature of the room, is measured, to determine its reduced volume v''. From the data obtained so far, we have for the contraction per unit of original gas;

$$c = \frac{1}{v}\,(v' - v'').$$

After this determination comes, if necessary, that of the water produced, which of course is practicable only if the original gas and the added oxygen were used in the state of perfect dryness and any added fulminating gas measured exactly. To determine the water—of which part in general separates out in the liquid form—the eudiometer is lifted out of the trough by means of a small beaker, and with it, as its temporary trough, placed within a glass cylinder through which a current of steam can be passed to raise the temperature of the whole to something like 100°C. The exact temperature t''' is noted down. If care be taken to arrange matters so that the pressure of the gas mixture produced is not more than 0·5–0·6 atmospheres the steam may be practically regarded as a perfect gas, so that the measurement of the mixture enables one to calculate its quantity. If the red. volume of the mixture be v''', we have for the steam per unit of original gas;

$$w = \frac{1}{v}\,(v''' - v'').$$

In this measurement the corrections for the expansion of the glass and mercury, which were referred to above, necessarily come in.

The determination of the carbonic anhydride produced is effected by caustic potash. In an aliquot part of the residue, the surplus-oxygen (or hydrogen if we have to deal with a gas combustible by hydrogen) is determined, if neces-

sary. Oxygen can be determined by explosion with excess of hydrogen (its quantity is $\frac{1}{3}$ of the contraction), or it may be determined by absorption with pyrogallate; hydrogen is determined by explosion with excess of oxygen, $\frac{2}{3}$ of the contraction is the volume of the hydrogen. The nitrogen is found by difference. The method of combustion—as a method of ultimate analysis at least—is susceptible of a high degree of precision, which, however, is attained only if we take care to avoid its numerous sources of error.

I. The reagents used must be absolutely pure, which of course includes absence of air; hence in any case the gas-evolution apparatus employed should be no larger than is absolutely necessary, so that the air-space is reduced to its minimum.

Pure *oxygen* is easily made. A few grams of pure potassium chlorate are introduced into a little bulb blown to the end of a glass tube, and the latter is then drawn out and bent into the form of a gas-delivery tube. The rest needs no explanation.

Pure *fulminating gas* is best produced electrolytically from 10 per cent. pure sulphuric acid. The two elements are sure to be produced in the exact ratio of $H_2:\frac{1}{2}O_2$, but whether the gas as it comes off really has this composition depends on the observance of certain conditions which cannot be formulated better than by a description of Bunsen's apparatus (Fig. 1).

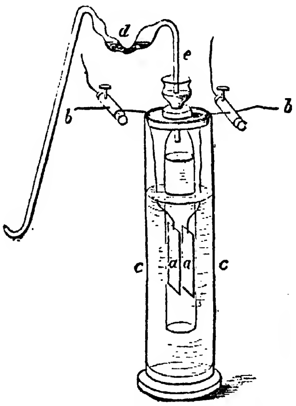


FIG. 1.

The decomposition-cell consists of a cylindrical bottle provided with fused-in platinum electrodes *aa*, and terminating in a funnel; it is filled with the acid up to about $\frac{4}{5}$ths of its capacity. The end *e* of the washing-bulbs and delivery-tube is ground into the neck of the funnel; a few drops of acid poured over the joint make it absolutely tight. The bulbs *d* are charged with a few drops of oil of vitriol to dry the gas evolved. The bottle is suspended within a bath of water *c c* (or alcohol to avoid its freezing in winter-time). To produce a current of fulminating gas, the wire ends *bb* are connected with the poles of a battery of four 'Grove' or 'Bunsen' cells, and the gas evolved during the first five minutes is allowed to escape in order to expel the air, and to establish absorptiometric equilibrium between the gas above, and the gas held in solution by the acid. As oxygen has a greater coefficient of absorption (β') than hydrogen (β''), the first portions of gas that come off contain an excess of hydrogen. Besides, the ratio $\beta':\beta''$ varies with the temperature; for this reason, and also to avoid undue heating of the conducting-wires, the bath is used.

Imagine the apparatus to be so modified that the oxygen electrode is immersed in a mass of liquid zinc-amalgam, which takes up the oxygen as quickly as it is liberated from water, and you have Bunsen's apparatus for producing pure *hydrogen*. But a sufficiently pure gas for most purposes can be obtained in the ordinary manner, namely, by the action of 10 p.c. (pure) sulphuric acid on pure zinc, in the presence of platinum, within a small, narrow-necked, flask. The hydrogen thus evolved is filtered through a short narrow tube full of fragments of caustic potash to remove traces of sulphuretted hydrogen and moisture.

II. The second point to be attended to is that the quantity of oxygen (or hydrogen) added to the gas to be burnt must be in excess over the calculated quantity (a *large* excess is not necessary). The mixture must be perfectly homogeneous before the spark is sent through it.

III. The gaseous mixture must be brought to a proper state of attenuation. Let us assume that the gas to be burnt is a pure specimen of H, CO, CH_4, or some other gas, C_xH_y. A glance at the formula shows how many volumes of oxygen we have to add to produce what we may call the respective fulminating gas. Thus the equation $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$, tells us that every one vol. of ethylene needs 3 vols. of oxygen. Any fulminating gas will explode when the spark is sent through it at the ordinary pressure, but the force of the explosion is in general more than the best eudiometer will stand. To avoid such accidents, we must attenuate the gas by addition of diluents (such as surplus oxygen or air), or by mere expansion, or in both ways. In practice we must go even beyond the safety point, because in most cases nitrogen is present even in the original gas, and a considerable quantity of this nitrogen may be converted into nitric acid if the temperature of the flame is too high. But we must take care on the other hand not to attenuate too largely, or else the mixture may miss fire, or, what is worse, suffer only partial combustion. The effect of an explosion—in the chemical, physical, and mechanical, sense—is determined by many independent variables, which, if arranged in the order of their importance, would begin with the chemical constitution of the gas to be burnt, and end with the relative narrowness of the eudiometer. But given a certain eudiometer, and suppose it to be charged with a certain fulminating gas which contains, let us say, unit vol. of the respective '*fuel*,' measured at the ordinary temperature and the pressure of one atmosphere, the attenuation of this gas to a certain eudiometer space, equal to λ units of vol., will render the explosion both safe and effective. λ of course has one value if the attenuation be produced by mere expansion (mere reduction of pressure), another value if it be produced—at, say, 1 atm. pressure—by

addition of air, a third, fourth, &c., in intermediate cases; each case fortunately admits of a liberal toleration, $\pm(\Delta A)$. The A for a given species of fuel can of course be determined only by experience; supposing it has been ascertained for H, CO, CH_4, and the value for CH_4 is A_0, we might suppose that the proper A for C_2H_4 or C_2H_6 would be about $2A_0$, that for a C_3-gas about $3A_0$, &c.; but unfortunately the supposition is not borne out by experience; C_2H_2, for instance, explodes far more violently than C_2H_4, although it contains less hydrogen per molecule. But to pass to experience. According to Bunsen and Kolbe, the explosion of ordinary fulminating gas $(H_2 + \frac{1}{2}O_2)$ in admixture with air takes its normal course at from 500 to 600 mm. total pressure, if the percentage of the explosive gas lies between 20·8 and 39·1. According to our calculation from the data of the five experiments recorded by Bunsen, this comes to the same as saying, if the partial pressure of the fulminating gas lies between 108 and 230 mm.; or if A, referred to the hydrogen, is between 4·9 and 10·5. If $A > 10{\cdot}5$, the gas fails to burn; if $A < 4{\cdot}9$, nitric acid is produced. In the combustion of a given quantity of oxygen by added hydrogen, we may use 3–10 volumes of the latter, per 1 vol. of oxygen, if we start with almost pure oxygen. In the analysis of ordinary air, 0·5 – 1 vol. of hydrogen per 1 vol. of air works well (Bunsen). Whenever hydrogen is used as a reagent, the chance of nitrogen being drawn into the combustion is relatively small, so that we have greater latitude on this score, in choosing our conditions. If the oxygen to be determined is accompanied by an unknown proportion of nitrogen, we first try two volumes of hydrogen for one of total gas; if the mixture fails to explode properly we add the requisite proportion of fulminating gas, *i.e.* so much of the latter that it forms about 40 p.c., but no more, of the whole, and explode again; this time presumably with success (Bunsen). In the case of marsh gas, Bunsen directs us to add 8–12 volumes of air besides the necessary 2 volumes of oxygen, which, assuming the mixture before the explosion to be at 600 mm., makes our A equal to 14 to 19. For C_2H_4, his directions are somewhat obscure, but in a test-analysis quoted by him, the pressure of the mixture as exploded was 546 mms., and it contained 0·04868 of its vol. of C_2H_4. Hence $A = 28{\cdot}6$; and the partial pressure of the explosive gas $(C_2H_4 + 3O_2)$ was 106 mm.

The addition of large volumes of air to the gas to be analysed does not of course add to the precision of the work generally, and in the best case will render the determination of the nitrogen in the ultimate product somewhat uncertain.

Thomas (*C. J.* 35, 213) was the first to substitute mere expansion for dilution; the (Frankland) apparatus he used enabled him to do this without trouble. Lothar Meyer and Seubert (*C. J.* 45, 581) have lately taken up the same method and rendered it available for Bunsen's apparatus by the invention of an auxiliary apparatus in which a kind of mercurial air-pump, constructed on the Geissler principle, serves to establish any desired pressure at the same time in the eudiometer and in a moist-vacuum barometer, so that the difference of level between the meniscuses of the two at once gives the pressure of the dry gas. By means of this apparatus, they ascertained, for each of a series of gases combustible by oxygen, the minimum pressure at which the undiluted fulminating gas is exploded by an electric spark, and also a range of pressures at which the explosion is both safe and effectual. The following table summarises what for us are the main results. To explain the headings let us give the reading of the table for CH_4 in full. Imagine a given quantity of marsh gas mixed with a little more than two volumes of oxygen; this mixture will explode normally if its pressure is reduced to $P = 140$ mm. by mere diminution of pressure, the partial pressure of the CH_4 itself will now be at 47 mm., and its attenuation (as defined above) at $A = 16$, that is to say, every 16 units of vol. of the expanded mixture contains 1 vol. of CH_4 measured at 760 mm.

Fuel	P (in millimetres)	p (in millimetres)	A
CH_4	140	47	16
C_2H_4	70–80, say 75	19	40·5
C_2H_2	40–50, say 45	13	59·1
C_3H_6	80	14·5	52·2
C_3H_8	80	13·3	57·0
CO	243–219	162–146	4·7–5·2
H_2	176–127	117–85	6·5–9
	(Partial Pressures.)		
[H_2	176–127	117–85	4·9–10·5]

[By Bunsen and Kolbe's experiments (*vide supra*); air added as diluent; *total* pressure in the mixture as exploded, 520–590 mms.]

With Meyer and Seubert's, or some other equivalent, apparatus at hand, the order of operations with a gas of unknown composition is as follows:—After having added a sufficient volume of oxygen, we next expand so largely as to be certainly on the right side of the safety line, and apply the spark; if no explosion occurs we repeat the trial at successively greater pressures. Should the greatest available pressure fail to produce inflammability, we add a suitable proportion of ordinary fulminating gas $(H_2 + \frac{1}{2}O_2)$ as above explained, &c., &c.

The Bunsenian mode of gas-analysis, while perfection in regard to precision and elegance, is very wasteful of time, for obvious reasons, which any reader who has followed us so far will easily discern. The desire to do away with this evil has led to the construction of quite a series of more or less complicated gas apparatus. The more important of these are described in the following paragraphs. To avoid repetitions, let us state beforehand that all the apparatus to be noticed agree in the following points:—

1. For accelerating the absorptions the reagents are all used as liquids, and the absorptions are carried out in a special piece of apparatus (*laboratoire*); the residual gas is then transferred to the *measurer*, where it is saturated with vapour of water, and measured.

2. The measurer is immersed in a water-bath to bring the gas contained in it to a definite constant temperature, without much loss of time.

3. The mode of measurement is so contrived that the calculation of the gas-quantities (the QS) becomes very easy or even unnecessary.

Regnault and Reiset (*A. Ch.* [3] 26, 333), while engaged in their great research on respiration, felt the want of a quick-working apparatus for the numerous gas-analyses involved, and at last adopted the combination represented in figs. 2 and 2*a*. The vertical tube A conjointly with the moveable trough V constitutes the

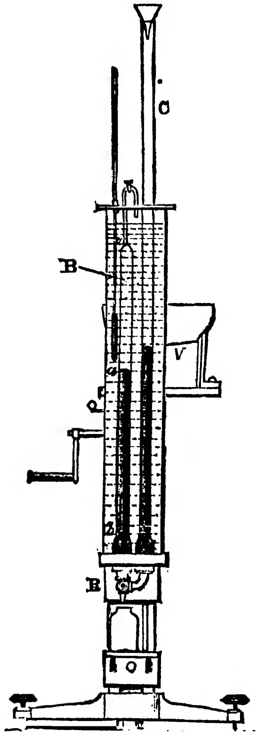


FIG. 2.

laboratory; the measurer consists of a long U-tube, the limbs of which are of glass, while the bend consists of an iron or steel tube, terminating in two sockets *b* and *c* (see auxiliary figure 3), in which the two glass tubes B and C are fixed by means of a resinous cement. A two-way cock R below B (fig. 3) enables one to effect the necessary connections. Tube B is provided with a couple of fused-in platinum wires near its top, so that it can be used for the combustions as well as for the measurements of the gases. Tube C conjointly with B serves as an open manometer. The capillary ends of A and B are cemented, each into the socket of a capillary steel stop-cock, and the ends of the two steel-fittings which face each other are shaped so as to constitute the two halves of a *Regnault'-coupling*, so that the two tubes can be united hermetically, or can be separated, at a moment's notice. The construction of a Regnault's coupling is seen from fig. 4. To unite A and B, the convex end of *r* (fig. 4) is smeared over with melted india-rubber, pressed against the concave part *a' b'*, and the two are then bound together by means of the clip *a''*. As the conical groove in *a''* has a slightly less angul[ar] aperture than the sharp welt which it go[es] over, if the two halves of *a''* are screwed again[st] each other, they exert a powerful pressure, an[d] make the joint absolutely tight. The volumete[r] B, in the original apparatus, had only o[ne] mark, somewhere about the middle; but th[e]

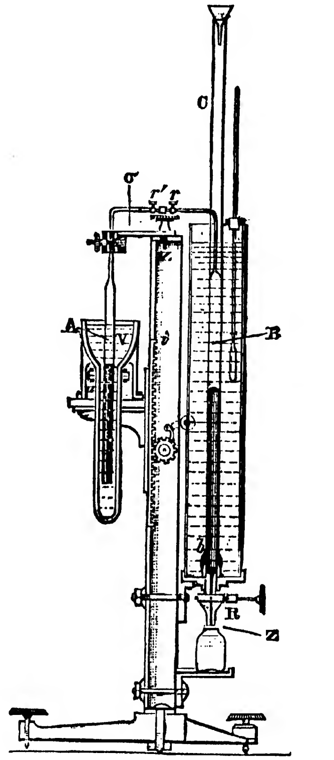


FIG. 2*a*.

inventors subsequently added two more, on[e] close to the upper end, and one near the lowe[r] for the measurement of exceptionally small, o[r] large, quantities of gas. The manometer C i[s] not graduated, as the apparatus is intended t[o] be used with a cathetometer; where this costl[y]

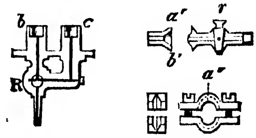


FIG. 3. FIG. 4.

instrument is not at hand, tube C must be pro[-]vided with a millimetre scale.

To prepare the apparatus for use it is place[d] on a substantial support not liable to incon[-]venient vibration, and the three levelling screw[s] of the stand are adjusted so that the tube[s] B and C stand vertical. To determine th[e] relative gas-volumes corresponding to the thre[e]

marks, the volumeter is filled with mercury, through C, and after the air-bells have been removed by the well-known artifices, the weights of mercury w_1, w_0, w_2, which the tube holds from its exit-end at r (fig. 2a) to the highest, middle, and lower, mark, respectively, are determined. For comparative measurements the volumes are put down as $\frac{w_1}{w_0}$, $\frac{w_0}{w_0}=1$, and $\frac{w_2}{w_0}$, respectively. In the absence of a cathetometer the level points of the three marks on the scale C must be determined with the help of an ordinary gas-room telescope. Lastly, a drop of water is introduced into B and spread over its surface. To analyse, say, a mixture of carbon dioxide, oxygen, and nitrogen, a sample of the gas is collected over mercury in A (perhaps with the help of an auxiliary-trough); tube A is coupled on to B (which is supposed to be quite full of mercury), and the gas is sucked into this tube by letting mercury run out at Z. B having been closed by shutting the cock r, communication is made with C, and mercury is run out until the meniscus in B stands at say exactly the middle mark; the final adjustment is made with the telescope when the temperature of the gas has certainly become equal to that of the bath. When the final reading is made, B must of course communicate with C only. The reading of the height h of the mercury column in C, counting from the respective mark up or down as the case may be, and the reading of the barometer, complete the measurements. Supposing h to be positive, and the barometer to stand at B, the gas-quantity measured is

$$Q=\frac{(v_0=1)\times(h+B-\pi)}{273+t}.$$

To absorb the carbon dioxide, the laboratory tube (which was left full of mercury) is charged with a little caustic potash solution, and the gas is blown into it from B. By letting the gas travel forwards and backwards between A and B a number of times, the absorption can be completed in a short time. The residual gas is then sucked back into B, care being taken to shut the cock r' as soon as the potash solution comes to some mark σ, in the capillary part of A. The thread of gas from σ to r which is thus lost is of no consequence, as it amounts to only $\frac{1}{5000}$ of v_0. The mixture of nitrogen and oxygen is measured as before. The rest requires no explanation. If all the several gases are measured at the same temperature and volume, the (dry) pressure P′, P″, P‴, of course may be taken as representing their QS (red. vols.).

Frankland and Ward, in 1853, introduced an ingenious modification of Regnault's apparatus, which differs from the original model chiefly in this, that the volumeter bears ten marks, so adjusted that the respective gas-volumes are to one another as 1 : 2 : 3 . . . . 10 exactly, and that in addition to Regnault's open tube C (Figs. 2, 2a), there is a third tube, D, which terminates above in a stoppered funnel or stop-cock. Tube D stands in the same water-bath with B and C; when used it contains only mercury and a little water, and thus assumes the character of a 'moist' barometer, which serves to directly measure the *dry* pressure of the gas shut up in B. Tube C (in F. and W.'s apparatus) serves only for the introduction of the mercury. The levels of the ten volumeter marks, in reference to the scale on the barometer, are of course determined once for all, hence the measurement of a gas, supposing its volume to have been adjusted to one of the ten marks on the volumeter, involves only one reading, namely that of the height of the mercury column in the barometer, which balances the (dry) pressure of the gas. Another advantage of F. and W.'s apparatus is, that for each gas measurement it gives one the choice among at least some three of the ten standard volumes, and thus enables one to reduce the error by an obvious method of repetition. Unfortunately, however, the barometer rather aggravates what in the original apparatus is a sufficient trouble, namely, the liability of the apparatus to get out of order. However carefully it may have been constructed, the joints between the glass tubes and their sockets are sure to become leaky, and the capillaries between the laboratory and the volumeter are exasperatingly fragile.

McLeod [1869] (*C. J.* [2] 7, 314), and Thomas [1879] (*C. J.* 35, 218) endeavoured to remedy these evils, and to effect other improvements. For details see the papers referred to.

Infinitely handier than Regnault's unwieldy machine, though not quite equal to it in potential precision, is

Doyère's Apparatus.—(First notice dates from 1848. Full description in *A. Ch.* [3] 28, 1.) The essence of Doyère's system is that the measurement of the gases is effected in a plain graduated eudiometer, while a series of Ettling's gas pipettes serves for the chemical treatment of the gases, and their transference from vessel to vessel. The Ettling gas-pipette is depicted in fig. 5, and a glance at the figure suffices to

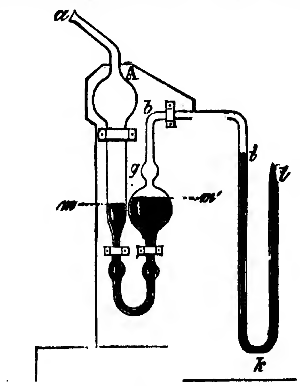


FIG. 5.

show, in a general way at least, how the instrument is used for the transference of a gas from one tube to another; nor is it necessary to formulate the conditions or limits of its availability. The measurer (fig. 6) when in use is suspended over a pneumatic trough, deep enough to admit of the total immersion of the measurer, and is surrounded by a mass of water contained in a cistern whose sides are of plate-glass, while the mercury of the trough forms its bottom. To

prepare the measurer for the reception of a gas, it is cleaned, slightly moistened inside, transferred to the trough by means of the portable mercury trap (fig. 7) fixed in the clip L, and filled with mercury by sucking out the air, by means of the U-shaped tube (fig. 8). The gas, which we will suppose to be contained in a gas-

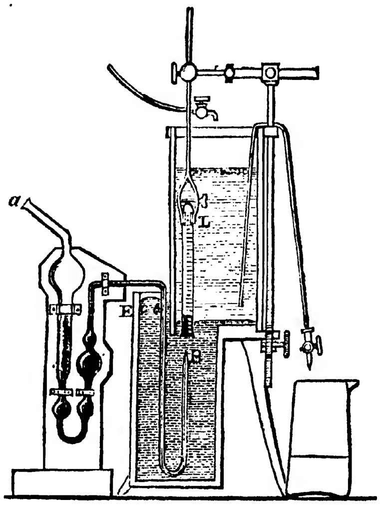


FIG. 6.

pipette, is then blown in, to be measured at a certain fixed disgregation, which is kept rigorously constant for the set of gas-quantities to be compared. A glance at fig. 6 at once suggests a mode of fulfilling this condition. But this mode is not Doyère's. He allows the tempera-

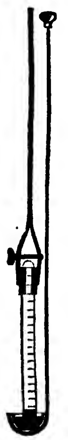


FIG. 7.

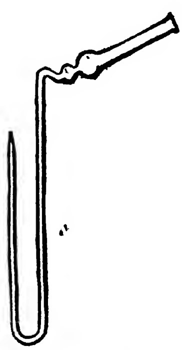


FIG. 8.

ture of the bath and the barometer to take care of themselves, but before each measurement he so adjusts the height of the water in the bath that the volume of a certain fixed quantity of air, shut up over water at a place within the water of the bath, assumes a certain fixed value, v_0. The standard body of air is contained in the '*Régulateur*' (fig. 9), a kind of air-ther-

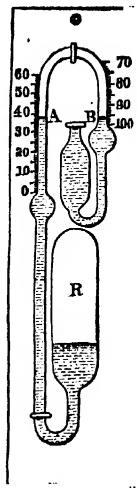


FIG. 9.

mometer which is fixed against a glass-plate, and, by it, suspended at a certain (by intention constant) height over the mercury-level of the trough. The water of the bath goes to some point B in the ascending branch of the capillary U-tube; BA is a thread of air; from A downwards there is a continuous mass of water, over which the standard body of air is shut up at R. Before each gas-measurement, the height of the water in the trough is so regulated (by means of taps) that meniscus A stands at some determined point of the scale, and the air which serves as regulator is consequently at some fixed volume v_0. This being done, the eudiometer is raised or lowered, until the height of the column of mercury suspended in it is at some fixed value, h_0. As a result, the gas is now practically at least, at a fixed disgregation.

Proof. The pressure of the gas exceeds that of the air of the regulator by $\Delta+p_s+h_0$, where Δ stands for the height of B 'over' A (we refer to the regulator), and p_s for the height from the level in the trough to that in R of the regulator—both reduced to mercury. With a properly chosen h_0, the value $c=\Delta+p_s-h_0$, if not nil, is at least small, and nearly constant. Now supposing we have, for two successively measured quantities of gas, I. and II.:

	I.	II.
For the regulator-air	V_0, T'; P'.	V_0; T''; P''.
For the gas . . .	V'; T'; $(P'+c)$	V''; T''; $(P''+c)$.

As the regulator-air is at the constant volume, v_0, we have

$$\frac{T'}{P'}=\frac{T''}{P''}. \qquad \text{I.}$$

The 'reduced volumes' (the Qs) of the two gases are

$$Q'=\frac{V'(P'+c)}{T'} \text{ and } Q''=\frac{V''(P''+c)}{T''} \qquad \text{II.}$$

and, as $\frac{c}{P' \text{ or } P''}$ is but small, we may write

$$\frac{Q'}{Q''}=\frac{V'}{V''}\left\{1+\frac{c}{P}\left(\frac{P''-P}{P''}\right)\right\} \qquad \text{III.}$$

As both factors in the second term with the bracket { } are very small, we have practically,

$$\frac{Q'}{Q''}=\frac{V'}{V''}.$$

As the measurer is necessarily very small, the adjustment of h_0 must be made, and the

gas-volumes read, with more than ordinary exactitude. Doyère accordingly provides a small short-vision telescope, which has a glass micrometer-scale (fig. 10) in its focus. The

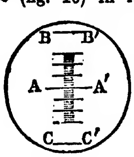


FIG. 10.

telescope is attached to a three-legged stand (which rests on a horizontal glass-plate fixed on the table close to the trough), in such a way that in all the necessary shiftings the optical axis remains parallel to, or when necessary, in, the same horizontal plane. To adjust h_0 the telescope is so focussed that it gives a distinct image of the mercury meniscus in the trough, which image is then made to coincide with line C-C' (or BB' if the telescope is an astronomical one). The eudiometer is then lifted or lowered until the image of the top of its meniscus touches the central line A-A', which assigns to h_0 a definite, though unknown, value. This adjustment being made, the telescope is drawn backwards a little on the glass-plate to afford a good image of the eudiometer-scale, and to enable one to read the volume of the gas. The

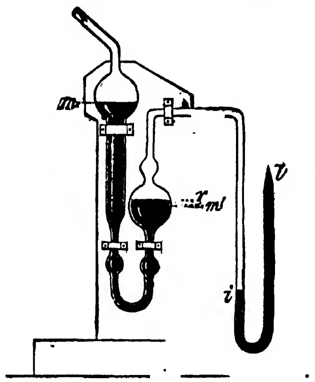


FIG. 11.

micrometer-scale serves to sub-divide the individual divisions on the eudiometer, which it does with an amply sufficient degree of precision. Before reading h_0 the eudiometer must be tapped to bring the mercurial meniscus into its normal shape.

Assuming now that a gas, measured as described, contained carbon dioxide and air, and that we wished to determine the carbon dioxide by absorption with caustic potash. We begin by charging a gas pipette with mercury to about the extent shown in fig. 5. We then take the pipette to an auxiliary trough, immerse its U in the well, and, after having blown out the air, suck in the requisite quantity of caustic potash solution from a test-tube inverted over the trough, taking care *not to let any more mercury follow than is necessary* (practically) to trap the contents by a thread of mercury *i l*. We then transfer the pipette to the measurer containing the gas (as indicated in fig. 6), press down the measurer over the outer branch of the U, and transfer the gas from the measurer to the pipette, by sucking at *a*, until drops of mercury are seen to fall into the working bulb, *but no longer*. Things are now in the condition depicted in fig. 11, and all that remains to be done is to agitate the contents gently so as to insure absorption of the CO_2, and then to return what is left of the gas to the measurer. This, however, is a delicate operation, which in the hands of a beginner is not unlikely to fail. The first step is to replace the pipette under the measurer, to lower the latter sufficiently (*v. infra*), and to blow into the pipette so as just to dislodge the mercury thread *i l*. Supposing the pipette contains no more surplus mercury over and above that which was in it at the beginning, then as long as the meniscus in the eudiometer is below or at a level with that of the mercury in the trough, as it is underneath the bath, only part of the gas will pass out of the pipette into the eudiometer. The second step is to lift the pipette, so that its outflow end, B (fig. 6) or *l* (fig. 11), becomes visible within the gas-space of the measurer. As long as it is there, and the pipette is kept vertical, whether the gas flows out of B, or in at B, or remains at rest, depends mainly on the pressure of the gas in the eudiometer, and consequently on the altitude of the latter. But this altitude we have under absolute control. Hence what we have to do is carefully and slowly to lift the eudiometer until the thread of liquid reagent which makes its appearance as soon as the bulk of the gas is out, has come to, say, 2 mm. from the outflow end. We then stop sucking, put the pipette down on the table (which of course at once seals the end B with mercury), suck at *a* until we see mercury dropping into the pipette, take the pipette out of the mercury, and put it on the table to have it at hand for a repetition of the absorption.

The sequence of operations described is not quite so easy in practice as it looks on paper, because success depends largely on the permanence of the position of the pipette in reference to the plumb-line. Tilting over the pipette in the direction of the U means adding to the pressure of the gas inside; and *vice versâ*.

For the explosions, Doyère provides a special stout pipette, with fused-in platinum wires, &c.; but the method of combustion finds little favour in his eyes, because his apparatus does not readily fall in with its requirements.

In conclusion, the writer may be permitted shortly to describe an apparatus of his own invention, which, thanks to the valuable assistance of Mr. Lennox, he was enabled to construct on his own premises, and which has since done him good service.

Dittmar's apparatus, like Doyère's, is based upon the Ettling gas-pipette. Apart from the necessary two troughs, it consists of the following three independent parts.

The *measurer* (fig. 12) is a combination of a wide with a narrow glass-tube, after the manner of Gay-Lussac's burette. The wide tube communicates by its lower contracted end

with a long capillary tube of india-rubber, and through it with a Geissler mercury-reservoir. At their upper ends both tubes are provided with Geissler stopcocks; to the exit-end of the wide tube is soldered the capillary U tube, volumes are counted from the point of the junction, because, after the introduction of a gas, the narrow canal firmly retains its thread of mercury. The measurer holds a fixed position on the right side of a pneumatic trough, A,

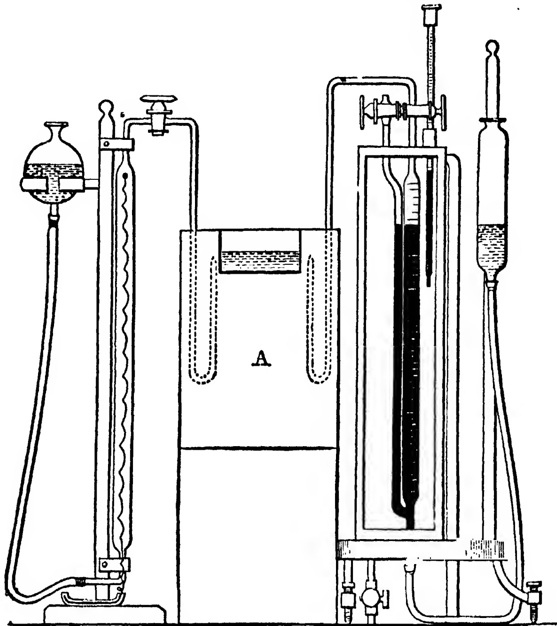


FIG. 13. FIG. 12.

characteristic of Ettling's pipette. The wide tube bears a mm. scale; the gas-volumes corresponding to the several marks are determined by gravimetric calibration, at a rigorously

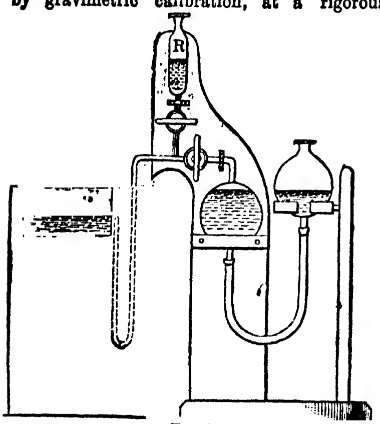


FIG. 14.

constant temperature, maintained by means of the water-bath. The narrow bit of tube between the top of the measurer and its stopcock is a capillary of the same bore as the U; it joins on quite abruptly to the wide tube, and the provided with two wells, one for the U of the measurer, the other for that of the exploder. In regard to the *exploder* (fig. 13), we have nothing to add to what is clearly seen from the figure, except the statement that the exploder in its present form is wider than the figure represents it to be, so wide, indeed, as to enable one to expand a gas considerably before exploding it.

The *absorber* in its original form is represented in fig. 14. For the interpretation of this fig. it suffices to say that R is a small mercury-reservoir which enables one to sweep out the thread of gas left in the capillary after the liquid reagent has been allowed to travel up to the safe side of the point of junction between the horizontal part of the capillary delivery tube and the stem of the reservoir. An improved form of the absorber (devised by Mr. Lennox) is represented in fig. 15.

To prepare the measurer for the reception of a gas, it is completely filled with mercury from the reservoir, the stopcock of the side tube is turned off as soon as all the air is driven out of it, and a drop of water is introduced into the main tube at a suitable stage.

The gas to be measured must be contained in a tube short enough to be within the range of the U: from this tube the gas is sucked into the measurer with the help of the reservoir, which is then adjusted so that the gas-pressure inside

is about one atmosphere. The stopcock at the side tube is then opened, and the height of the reservoir is re-adjusted so that the menisci in the narrow and wide tube are in the same horizontal plane. A horizontal wire in the telescope facilitates this adjustment materially, but is not indispensable. The gas is now at the pressure $B + b - \pi$, where B is the height of the barometer, π the pressure of the vapour of water, and b the excess of the capillary depression in the narrow side tube as compared with that in the wider branch. The temperature is of course that of the water-bath. As both P and T oscillate with a series of measurements only

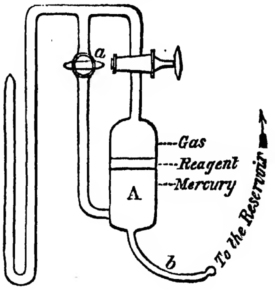


FIG. 15.

within small amplitudes, it is expedient to reduce, not (for instance) to unit disgregation, but to some mean pressure and temperature (if there has been any variation in either or both) by means of some suitable formula, such as:

$$V_0 = V\left\{1 + \frac{(\Delta P)}{P_0} - \frac{\Delta T}{T_0}\right\}$$

where P_0 and T_0 stand for the standard values, and the observed values are assumed to be greater than these by (ΔP) and (ΔT) respectively. If a table of the reciprocals of the practically occurring PS and TS is at hand, the calculation becomes so very easy that it is not worth while to set up a disgregation indicator.

Technical Gas-Analysis.

To meet the demands of chemical industry there has been invented a variety of methods for the rapid, though perhaps only approximate, analysis of certain classes of gas-mixtures. The methods all agree in this, that the use of mercury is dispensed with, the gases being measured over water, or even perhaps over the respective absorbent solutions. The Bunte *Gas-burette* may be quoted as a typical example of this class of apparatus. Imagine a long cylindrical pipette graduated for gas-volumes and provided with a stop-cock at each end, and combinable with a reservoir by means of a long india-rubber tube. To analyse, say, a chimney-gas, the burette is filled with the gas by displacement, and the reservoir, after having been filled with water, is attached below. By placing the reservoir at a certain convenient altitude, and temporarily opening the upper cock, a certain volume of the gas is shut off at the pressure of one atmosphere. In order now to determine the carbonic acid, we suck out the water by an (easily imagined) auxiliary apparatus, and replace it by a solution of caustic potash, which is shaken with the gas. The caustic potash is then sucked out, water is let in, the original pressure is re-established, and the residue is measured. In a similar manner, the oxygen is determined by absorption with alkaline pyrogallate.[1]

ANALYSIS BY THE METHOD OF TITRATION.

This branch of analysis comprises the applications of what was described in a previous section as the *titrimetric method of indirect weighing*. The method in any of its present forms is applicable only to such reactions as proceed readily in aqueous solutions; the reagents, accordingly, are always used in the form of *standard solutions* (*liqueurs titrées*), *i.e.* solutions the strengths of which are known in reference to the process under consideration.

The amount of standard solution required in a *titration* may be measured either by weight or by volume; in either case the measurement of the solution is only an indirect mode of weighing the active agent contained in it. The gravimetric method is certainly susceptible of the higher degree of precision; yet the volumetric method is universally preferred, because it is by far the more handy and expeditious of the two, and, if properly conducted, (with very few exceptions) does ample justice to even the best titrimetric processes.

The invention of volumetric analysis must be credited to Gay-Lussac. Long before him, it is true, Stirling enunciated the principle of the method, and Vauquelin and Descroizille used it for assaying commercial alkalis; but to Gay-Lussac undoubtedly belongs the credit of being the first to bring the method into an exact form, and to work out all its technicalities in the most masterly manner. Volumetric analysis was slow in progressing. Gay-Lussac's more immediate successors, misled by his success in regard to silver, directed their attention almost exclusively to the translation of established gravimetric into volumetric methods; failing to see (what is now so obvious) that the number of reactions to which both methods are applicable must necessarily be very limited.

Very little real progress was made until 1856, when Bunsen, by introducing a new idea, gave a fresh impetus to investigation. Starting from the well-known reaction which takes place when iodine solution is dropped into aqueous sulphurous acid (and which Langlois had already utilised for the determination of this substance), he established the conditions under which the process takes the precise course indicated by the equation; and on the basis thus gained he developed exact methods, not only for the direct determination of these two bodies, but also for the indirect determination, by means of the same two solutions, of a whole

[1] Professor Winkler, of Freiberg, has made a special study of this branch of gas-analysis, and has written two excellent books on the subject; one of these has been translated into English by Professor Lunge. To these books and another we refer for further information. (1) Dr. Clemens Winkler, *Anleitung zur chemischen Analyse der Industrie-Gase* (Freiberg, Engelhardt, 1876). (2) An abridged edition of the same by the author. Translated by Lunge (Van Voorst, London). Also, *Neue Methoden zur Analyse der Gase*, von Walter Hempel (Braunschweig, Vieweg u. Sohn, 1880).

series of oxidising agents, for which an equivalent of iodine can be substituted by the purely qualitative execution of certain reactions.

By this memorable research volumetric analysis found its true sphere of action, as an invaluable means for the determination of *generic* radicles, such as the active oxygen in peroxides, the loosely held chlorine in perchlorides, the replaceable hydrogen in acids, the oxygen or chlorine-equivalent of reducing agents; for a host of determinations, in short, which practically lie outside the range of the gravimetric method. Where the two methods compete in the solution of the same problem, volumetric analysis generally offers the advantages of greater promptitude and facility of execution; it, indeed, stops where with gravimetric analysis the most difficult part of the work would begin. This advantage, however, is not an absolutely clear gain. The volumetric method, so to say, does not look at the *body* to be determined, but, in a somewhat blindfolded way, only measures one of its chemical properties, which in no case appertains to that body only; hence errors are more likely to be overlooked, and are far more difficult of subsequent correction, in volumetric, than in gravimetric, analysis; for gravimetric analysis furnishes the thing to be weighed in the form of a definite compound, which can be examined for its purity, and, if necessary, be purified before it is weighed. A small amount of iron, nickel, zinc, &c., which has escaped precipitation may be searched for in the filtrate and recovered; any deficit or excess obtained in a titration is thrown away with the rest of the products.

We have no space for a full history of our subject; yet we must not forget to give credit to the late F. Mohr for having contributed largely to the modern development of volumetric analysis, by his criticisms of old, and his invention of new, methods; by the construction of useful apparatus; and last, not least, by the compilation (for the first time) of an original and comprehensive handbook[1] on the subject.

In now passing to the systematic exposition of our subject, we will begin with a few remarks on the

Graduated Glass Measures

which serve for the preparation of the standard solutions, and the necessary measurements of liquids generally. Volumetric analysis of course involves only comparative measurements; we indeed never measure a standard solution otherwise than in reference to itself; hence the unit of volume may not only be chosen at pleasure, but need not bear any known relation to the unit of weight. But the only correct mode of gauging a liquid measure is to determine the weight of water it holds (or delivers); hence for those who are in the habit of using the gram as their unit of weight the most convenient unit of volume is the volume at (let us say) 15°C. of that mass of water whose *uncorrected* weight in air is one gram. We might herewith adopt this unit and call it the '*fluid gram.*' In doing so we should not be guilty of any innovation. The customary unit with most chemists and instrument-makers, it is true, is the *cubic centimetre*, but it is this only nominally; the actual unit in almost all commercial '*cubic centimetre*' measures comes nearer to our fluid gram than to the nominal unit. From what we have said, the reader will understand that if in the sequel we speak of *cubic centimetres*, or *litres*, these terms mean only *unit-volume*, and 1000 *unit-volumes*, respectively, unless it is clear from the context that we mean to approximately define an absolute quantity, or to refer to the well-known relation between the *litre* and the *kilogram*.

As all aqueous liquids wet glass, the mark on a *litre flask*, &c., can be correct only in reference to a specified mode of reading. The best mode is this. Place the vessel so that its axis is vertical, and look at the meniscus horizontally with one eye. The meniscus then appears as a flat crescent-shaped strip. The lower boundary of this strip is taken as the line of reference, and the real, or imaginary, mark on the graduation with which it coincides (visionally) is taken down as the *reading* of the liquid. The line referred to gains in sharpness of definition if it is observed in transmitted light, and a strip of black paper is fixed to the back of the measure about 2–3 mms. below the line. With only one of the customary standard solutions, namely the almost opaque solution of permanganate of potash used for iron titrations, this mode of reading does not work. In the case of this liquid we must take the upper boundary of the meniscus as our reference mark; this upper boundary assumes its maximum definition if viewed in reflected light, and with a white background (a piece of paper) immediately behind it. Any reading made in this exceptional manner is of course subject to an obvious correction, the amount of which is ascertained by measuring the height of the meniscus of a transparent solution in the same vessel. In most cases, however, the volume to be determined is the difference between two consecutive readings, so that the correction in question becomes unnecessary.

In a vessel which serves for measuring out a certain volume, the small quantity of liquid which permanently adheres to the glass must be allowed for by the maker, *i.e.* the scale must be constructed so as to include what would otherwise be a necessary correction. In the case of graduated pipettes this can of course be done only on the basis of a conventional mode of emptying out, which, when once fixed upon, must be rigorously adhered to. The thermic expansion of glass may unhesitatingly be neglected in the graduation of a titrimetric measure. A glass flask which holds 1000 c.c. at 15°C., at 15 ± 10° holds 1000 c.c. ± 0·27 c.c.; *i.e.* only $\frac{1}{4000}$th more or less. The thermic expansion of the solutions measured is far more considerable, and cannot in all cases be neglected. We shall come back to this point in the next section.

The chemist now-a-days has no occasion to graduate his own burettes, litre-flasks, &c., but he should never use a set of instruments—although they come from the most famous maker—without having first tested them. The following is the method to be pursued. Passing from measure to measure, and with each measure from mark to mark, measure in or out the several marked off volumes of pure water of

[1] Mohr, *Lehrbuch der chemisch-analytischen Titrirmethode.* The first edition dates from 1857; the fourth and last from 1886.

known temperature, and determine their weights in grams. In the case of apparatus with a running-on scale, only every 10th or 20th mark need be checked in this manner, unless there are visible irregularities in the graduation. After having thus gone through the whole system, reduce all the water-weights to the same temperature, say to 15°C. (*i.e.* from the observed weight of water of $t°$ calculate the weight of water of 15° which fills the same space); divide each corrected weight by the corresponding nominal volume, to find the weight-value of the actual unit—and draw your conclusions. Supposing the several units agree fairly, select a suitable average value (not necessarily the mean, because the numbers are not all of the same weight mathematically) as *the* unit, and calculate the volumes corresponding to the several marks in terms of this adopted unit. The results ought, by theory, to agree with the respective nominal values, but in practice, of course, we cannot expect absolute coincidence. In a burette, for instance, which gives $\frac{1}{2}$ c.c.s directly, we must tolerate $\pm 0{\cdot}1$ c.c., and with the lower marks, even a little more. Whether the actual unit is, or is not, equal to the nominal is of no consequence; yet, if it is not, it is obviously advisable to note down its value—in fluid grams or c.c.s—for future reference.

To facilitate the calculations involved in such work as the graduation of instruments, the writer many years ago calculated the following table:—

A mass of water, which, in air of t°C., and 760 mm. pressure, balances a brass kilogram weight, at t°C. occupies $(1000+x)$ *fluid grams* = $(1000+y)$ *true cubic centimetres.*

$t°$	x	y	$t°$	x	y
+ 0°	−0·64	+1·25	+15°	+0·00	+1·89
4	0·78	1·12	16	0·15	2·04
8	0·68	1·21	17	0·30	2·20
9	0·63	1·27	18	0·47	2·37
10	0·56	1·34	19	0·66	2·55
11	0·47	1·43	20	0·85	2·74
12	0·38	1·52	21	1·06	2·95
13	0·27	1·63	22	1·28	3·17
14	0·14	1·76	23	1·51	3·39
15	0·00	1·89	24	1·75	3·63

Preparation of Standard Solutions.

In fixing upon the degree of concentration for a specified standard solution, we may allow ourselves considerable latitude. As a rule the nature of the volumetric process for which the solution is to be used may be left out of account; all we need look to is that the probable inherent error of the method corresponds to a distinctly visible difference of level in the burette; say to 0·1 or 0·2 c.c. according to the size of the 'c.c.' With methods possessing a very high degree of inherent precision this rule would lead to an inconveniently dilute reagent. In such (rare) cases we help ourselves by supplementing a moderately dilute standard solution with a *decimal solution*, meaning a solution prepared by diluting the reagent proper with water to 10 times its volume. The decimal solution serves only to finish the titration which has already been almost completed by means of the standard solution proper. This system of course is a mere delusion unless the stronger solution be measured with at least 10 times the precision attained with the decimal one.

The strength of any given solution should be so defined as to reduce the subsequent calculations to their highest degree of simplicity. Supposing, for instance, we have to deal with a standard sulphuric acid intended for the measurement of alkalis; evidently it would not be expedient to note down the number, n, of grams (or mgms.) of H_2SO_4 or SO_3 which is contained in each litre (or c.c.) of the reagent. As the number when calculated into KHO, NaHO, Na_2CO_3, &c. has always to be divided by $SO_4H_2(=98)$ or by $\frac{1}{2}H_2SO_4(=49)$, it is obviously better to calculate the value $\frac{n}{49}=\tau$ (as a decimal) and put down this τ as the strength of the solution. Were the solution intended exclusively for the determination of soda, to be reported as Na_2O, it would be still better to calculate the value of $\frac{n \times Na_2O}{H_2SO_4}=\tau'$, and note down the weight τ' (of sodium monoxide) as the strength of the reagent.

For the standardisation of a specified solution we have in general the choice between two methods; (1) a quantitatively exact synthesis; (2) an approximate synthesis, followed by an exact analysis. The first method may assume one of two forms; we either weigh out exactly so much of the pure reagent, dissolve it in water, and dilute to, say, 1 litre; or else (if the pure reagent is not itself at hand) we analyse, say, a strong solution of the pure or impure reagent, by means of some very exact method, and synthesise directly on the basis of this determination. In regard to the second method, the first step of course is to procure an approximately correct solution. For example, let us assume we wish to prepare a standard hydrochloric acid containing exactly HCl = 36·5 grams per litre. An apology for such a solution might be obtained from the ordinary (pure) laboratory acid, by determining its specific gravity, deducing the percentage, and synthesising on the basis thus gained. In all such cases it is expedient to so allow for the uncertainty in the assumed percentage that the solution obtained is sure to be *stronger* than intended. In accordance with the rule, let us assume the actual strength, as found by analysis, to be p, instead of the intended strength p_0, and let $p>p_0$. Obviously our 'v' litres of reagent must be diluted to $\mathrm{v}=\frac{vp}{p_0}$ to bring the strength down from p to p_0; the liquid must not be diluted with $v\left(\frac{p}{p_0}-1\right)=w$ litres of water, because the two liquids when mixed would contract, and a little more than w litre, say $(1+\epsilon)\,w$ litre, of water would be necessary to bring up the volume to the intended value, v. In practice, however, large volumes (such as we assume our v and v to be) cannot be measured with adequate precision, so that the second (theoretically faulty) method is generally the better of the two. It certainly is the better if the required correction is only small; if for instance $\left(\frac{p}{p_0}-1\right)$ is something like 0·03 or less. In such a case, if only

w as calculated is measured accurately, the corrected solution will be as near the intended strength, p_0, as the given solution was near its strength p.

As an example, let us take $\frac{p}{p_0} - 1 = 0{\cdot}03$; $v = 10$ litres; $\delta v = \pm 0{\cdot}5$ litre (which is a liberal allowance); and we have

$$\frac{\delta p_0}{p_0} = \frac{\delta p}{p} \pm 0{\cdot}0015.$$

Even in such a case it is only prudent again to analyse the corrected solution, to see that no blunder has been made. Supposing (to return to the example) the number p had been the result of three well-agreeing analyses, the intended value for p_0 had been 37·00, and the analysis of the corrected solution had given for p_0 the value 36·84; the most probable value for the actual strength would be $(3 \times 37{\cdot}0 + 36{\cdot}84) \div 4$.

Turning back, let us now assume $p_0 > p$. In this case our v litres of solution should be reduced to $\frac{p}{p_0}v$ litres, by elimination of $(1+\epsilon)\left(1 - \frac{p}{p_0}\right)v =$ '$(1+\epsilon)\,w$' litres of water. Even where evaporation would be permissible, it is better to compensate for the surplus water by addition of the substance which served to make the solution. Supposing we had used s grams of substance for every 1 litre of reagent produced. Clearly $\frac{p_0}{p}s = s_0$ grams is what ought to have been taken. One way then is to prepare some (say $\frac{1}{4}$ litre) of the solution by means of the corrected method and to determine its specific gravity, π_0, in order to be able to reduce to weight; thus:

1 litre of solution (p_0) . . . $= 1000\,\pi_0$ grms.
Weight of substance in it . . $=$ s_0
Hence weight of the water . . $= 1000\,\pi_0 - s_0$

Or every gram of water requires

'c' $= \frac{s_0}{1000\,\pi_0 - s_0}$ grms. of substance to be converted into solution of the intended strength, p_0; hence our $v \times (1-\epsilon)\,w \times$ kilos. of water require $v \times (1+\epsilon)\,wc \times$ kilos. of substance. All that we need for the calculation of $(1+\epsilon)w$ is the specific gravity π of the uncorrected solution. Obviously $(1+\epsilon)w = 1000(\pi - \frac{p}{p_0}\pi_0)$ grams. In practice, however, it is scarcely advisable to go to all this trouble. It is easy by some short cut (based on the above) to name a number of grams of substance, which if added to one litre of solution would bring up the strength to a little above p_0. Suppose the increase of volume involved in adding these grams of substance is less than, say, 0·1, 0·2..., say y litre. Then, to set things right, we calculate the correct mass of substance for $1+y$ litres, which is $(1+y)\,\frac{p_0}{p}s$, weigh out what this mass is more than the s grams present, in each litre, add this to each litre of solution as given, and dilute to $1+y$ litre by addition of water. If p differs much from p_0, it is expedient to slightly over-correct the solution, to determine the exact value, p', which the solution now has, and (if $p' > p_0$ as intended) to correct the strength, by dilution, as explained above. If p is only a little less than the intended value p_0, we may safely assume the surplus water per litre to be $1 - \frac{p}{p_0}$ litre, and add the exact weight, x, of substance, which by calculation converts the small quantity of water into correct solution. The result (in the absence of blunders) will be quite correct even if v was only approximately measured, because a very small volume of water added or withdrawn from the total of v litres would make the solution absolutely correct (apart from the error in p of course). One point remains to be considered. Supposing the strength of a solution at t_0 degrees is p_0, what is the strength p_1 at t_1 degrees? It would not do to calculate the correction from the expansion of pure water from t_0 to t_1, because all standard solutions expand more largely than pure water does. A correct method is to determine the specific gravity (say the weight contained in a narrow-necked 100 c.c. flask) of the solution at t_0 degrees and at t_1 degrees. Supposing the weight of it is π at t_1 and π_0 at t_0, we have $p_1 = \frac{\pi_1}{\pi_0}p_0$.

This correction of course is indicated only in the case of very exact methods. But in their case it is best altogether to eliminate the uncertainties of volume-measurement by effecting the final standardisation by volume and by weight at the same time; by determining for instance at the same time the weight in grams and the volume in c.c.s of the quantity of standard nitrate of silver which is required for the exact ppn. of (say) $\frac{KCl}{100}$ grms. of pure chloride of potassium. This need not hinder one in so adjusting the solution that the quantity referred to may for all ordinary purposes be assumed to be equal to 100 c.c. For the purpose of a highly exact determination, the bulk of reagent (*e.g.* $AgNO_3$ solution) required, after having been measured out, is weighed into the (chloride) solution to be analysed, and the small excess of substance or reagent left is determined by volumetric titration with decimal solutions.[1]

The adjustment of an analytically standardised solution to an exact pre-determined strength is advisable only if the solution is permanent, and is meant to be used very frequently, otherwise it is better to note down the strength as it is, and calculate from it. A solution known to contain $1{\cdot}023 \times HCl$ grams per litre is almost as convenient as one containing $1 \times HCl$ exactly. Because for one or two analyses we can well afford to calculate, say, the product $1{\cdot}023 \times \frac{Na_2O}{2}$, and for a very long series of such determinations the value may be calculated once for all and noted on the label.

On the Theory of Titration.

Let A and B be two chemical species, which, when their solutions are mixed together, combine with, or decompose, each other in some definite manner. Is the reaction available for the mutual volumetric measurement of A and B, or (let us rather say) for the measurement of A

[1] Compare Dittmar's *Memoir on the Composition of Ocean Water*, 'Challenger' Memoirs, page 4; also his *Exercises in Quantitative Analysis*, section on *Sea-water*.

by B? It *may* be if, under easily realisable conditions, it proceeds rapidly, and, if it is possible under these conditions to recognise the *point of saturation* with sufficient sharpness, *i.e.* the point from which onwards an additional drop of B-solution does not produce a recognisable change. In some cases the point of saturation defines itself naturally by coinciding with some sudden visible change, *e.g.* a change of colour. It does so, for instance, if the reaction is a double decomposition, $a+b=c+d$ (where a, b, c, d, stand for definite relative quantities of the reagents A or B, and the products C and D respectively), and if A (or B) is intensely coloured, while B, C, and D (or A, C, and D) are relatively colourless, or at least do not hinder the observation of the colour of the last remnant of A, or a slight excess of B.

Examples: 1, Oxidation of ferrous salt (A), by permanganate (B), with formation of ferric salt (C), and manganous salt (D).—2. Decolourisation of the intensely blue solution of cupric-ammonium salt (A), by the reducing action of (standard) cyanide of potassium (B), with formation of colourless double cyanide of copper and alkali metal (C), and cyanate and other salts of alkali (D).

Sometimes when such colour-changes do not occur, they may be produced by addition to the solution to be titrated of a suitable *indicator.* Thus: 1. Litmus solution may serve as an indicator in the volumetric neutralisation of acid by alkali (or *vice versâ*).—2. Iron-alum may serve as an indicator in the determination of silver (salt) by added sulphocyanide of ammonium, the red colour of $Fe(NCS)_3$ becomes permanent only when all the silver has been ppd. as AgNCS, and a slight excess of sulphocyanide has been added. The indicator in this case would evidently be of no use if it were not the case that $Fe(NCS)_3$, which is produced locally from the first, is decomposed as readily and in the same way by silver salt as the alkaline sulphocyanide is. A similar remark applies to indicators generally. If an indicator, while otherwise trustworthy, fails only to fulfil the condition stated above, it may still be available in the sense that, instead of adding it to the 'A'-solution from the first, we may apply a little of it to drops of the mixture taken out at suitable stages in the process of the reaction. Thus, for instance, in the titration of phosphate (A), by uranic acetate (B), prussiate of potash may serve as a *drop-reagent,* because, although unavailable as an indicator proper, if added to a drop of the mixture it produces the red-brown colour of ferrocyanide of uranium only if the uranium is present as (an excess of) acetate; the uranic phosphate is not decomposed by the prussiate. The action of an indicator need not necessarily consist of a colour-reaction; a ppn. if sufficiently delicate, is as good in principle, though not as a rule in practice because the locally-formed characteristic pp. will not disappear so readily on stirring up as the colour of a dissolved product would.

If the reaction is a steadily progressing ppn. of the essential radicle a in A by B, the end of the reaction of course coincides with the completion of the ppn., *i.e.* the point when (supposing B to be added in successive drops) the last remnant of a has just been thrown down by the n^{th} drop of B, so that the $(n+1)^{st}$ drop fails to give a turbidity. For such reactions we need no indicator or drop-test, although such may be very convenient.

As soon as we have found some means for recognising the end-point in our reaction with sufficient sharpness, we can decide the question as to its availability by preparing standard solutions of A and B respectively, and determining the ratio $a:b$ corresponding to the end-point under a sufficient variety of conditions. In a first series we work with the plain solution, but take care in one set of trials to begin with A and drop in B until the reaction is apparently completed; and in another set of trials we begin with B, pour in a slight excess of A, and then finish with B; this is done in order to see whether the ratio $a:b$ is independent of the mode of mixing. In a second series, we add known, but varying, proportions of water. In a third series we add more or less (but always a known weight (x) of this or that body X which in the practical application of the method would be likely (if not sure) to be present, &c. From Series I. and II. we easily calculate the small excess of reagent B which must be added, per F c.c. of total mixture at the end, to produce a visible end-reaction. We then calculate for each trial the value $K=\frac{V_b-\beta F}{V_a}$, and see whether there is a practically sufficient and available area of experimental conditions within which the ratio $a:b$ has a constant value. Or, what comes to the same thing, we take the mean of all the Ks (let it be $=K_0$), and see whether the values of V_b as calculated by the equation $V_b=K_0V_a+\beta F$ agree sufficiently with the directly observed values. Should this not be the case, the process need not necessarily be given up as hopeless; it may still remain worth while to see whether agreement between theory and practice cannot be established by adding a term cx to the right side of the equation, where x stands for the weight of some subsidiary component X, and c is a positive or negative constant, whose value must of course be experimentally ascertained. In such cases, however, it is better to leave the chemical significance of K_0, β, and c, entirely on one side, and to calculate them as so many empirical coefficients from the sum-total of the results. A formula thus obtained is of course of no practical value unless β and c are so small that an approximate determination of F and X suffices for an exact calculation of the respective terms. As an illustration we may quote Liebig's method for the determination of urea (A), in presence of chloride of sodium (X), by means of standard mercuric nitrate (B) as a pptnt. of the urea, and carbonate of soda as a drop-test for excess of pptnt. The exact volume V_b of mercuric nitrate solution (*i.e.* weight of HgO) to reach the end-point for a given weight (a) of urea, varies with the dilution, F, and the weight X of salt present; but V_b is[1] in sufficient accordance with equation $V_b=ak+\beta F+cx$, whose constants have been determined (virtually) by Liebig.

Nothing said so far is based on the presumption

[1] Or at least is supposed to be.

that the exact chemical theory for the reaction between B and A is known. There are indeed a number of useful volumetric processes which are based upon unexplained, or only half-explained, chemical reactions. Fehling's method for the determination of glucose affords an illustration. If a dilute solution of glucose is dropped into a hot, strongly alkaline, solution of tartrate of copper (CuO) and potash, the CuO is reduced to (a pp. of) Cu_2O, the blue colour of the solution disappears, and the sugar suffers some unknown kind of oxidation. Yet the ratio between (say) dextrose oxidised and copper-oxide reduced, under specified conditions, is fairly constant, and the reaction is accordingly available for a fairly exact method for the determination of dextrose.

The well-known process of Clark for the determination of the hardness of a water by means of standard soap might be quoted as another example. But such purely empirical processes, however useful they may be for this or that practical purpose, are of little importance as auxiliaries of exact analysis, which demands of a titration-process in the first instance that in any given case the question of its applicability can be decided *a priori* with at least a high degree of (if not with perfect) certainty. And this is possible only if the process is based on a definite chemical equation which gives a qualitatively and quantitatively exact account of what is going on.

From the fact, however, that some equation, $a+b=c+d$, is in itself a correct theory of the action of A on B as resulting in the products C and D, it does not follow that the equation is a sufficient theory of the corresponding process of titration. Because experience shows that, in general, ready-made C and D when mixed together produce A and B in accordance with the inverse equation $c+d=a+b$. Hence supposing we start with a parts of A and add more and more of B, the *end reaction* is reached only when a part (say qa) of A is transformed at the expense of qb parts of B, while $(1-q)$ times $(a+b)$ are still present in their original condition. Generally, q is a continuous function of the experimental variants (state of dilution, temperature, &c.), and the translatability of the reaction into a titrimetric process depends on the possibility of finding a sufficient area of conditions within which q is, at least practically, equal to unity.

If one of the products (C and D) separates out as an absolutely insoluble pp., or escapes as a gas, the reverse reaction does not occur, and q becomes equal to unity; the *apparent* end-point is the *real* end-point of the reaction. Hence we should think that ppns. (we mean cases where that radicle in A which is really the thing to be determined, by uniting with the essential radicle in B, separates out as a pp.), should be pre-eminently suitable for volumetric application. Experience, however, shows that the reverse is true. Because in the majority of cases the pp. carries down more or less of one or other of the other reagents or products, and so disturbs the quantitative relations. Very often also a considerable excess of pptnt. is required to produce complete ppn. within a reasonable time. Both difficulties (for example) present themselves in the case of that reaction, $BaX+SO_4R_2=R_2X+BaSO_4$, which is so largely used for the gravimetric determination of SO_4 and of Ba. The irregularities referred to[1] can be set right (more or less easily) in the gravimetric application of the reaction; to the volumetric application they are absolutely fatal. The number of ppns., indeed, which afford a basis for correct volumetric processes is extremely limited.

Certain classes of double decompositions and oxidations, in which reverse reactions are prevented by the great inherent stability of one of the products, are admirably adapted to volumetric processes. To give examples:

Any strong acid, XH, when mixed progressively with a solution of some strong base of the type ROH (ex. KHO,NaOH,$Ba(OH)_2$), is ultimately converted into normal salt, XR, with formation of that highly stable substance water. The general reaction is $XH+ROH=RX+HHO$, and the end-point can in all cases be sharply defined by means of a few drops of neutral litmus-solution as an indicator. Hence any acid (or rather the 'H' in any acid) may be accurately measured by means of a standard solution of, for instance, caustic potash; and any of the bodies ROH (or rather their 'OH') by means of a standard solution of (say) hydrochloric acid. The latter method applies almost directly to the (soluble) carbonates, sulphides, cyanides, &c., of the alkali metals. All the carbonates &c. referred to can be measured indirectly by the combined application of the two standard solutions: we add first an excess of standard acid, and heat to expel the volatile acid (CO_2,H_2S, &c.), then colour with litmus, and titrate back with standard alkali, till the point of neutrality is exactly reached. By substituting *aurine* (in alcoholic solution) for litmus, the method becomes available also for magnesia (Tornö); and by using nitric acid as the standard XH, we can determine even oxide of silver (Dittmar).

What we said of carbonates, &c., in reference to the metallic radicles, R, holds for the ammonium salts of our acids, XH. To determine, for instance, HCl or H_2SO_4, in the presence of ammonia (as the only base), we need only add a known excess of standard alkali, expel the liberated ammonia by evaporation, then add litmus, super-saturate by standard acid, boil off the carbonic acid, titrate back with standard alkali until the point of neutrality is exactly reached, and balance the equivalents of base and acid used as reagents, against each other; the balance of base-equivalents measures the acid given for determination.

That this method of acidimetry applies also to cases where the base can be separated out by excess of standard alkali, as an acid-free pp., is obvious. Oxide of copper (given as $CuSO_4$ or other cupric salt) fulfils this condition in the sense at least that the acid ppd. at first as part of a basic salt, can be re-extracted by boiling with excess of alkali.[2]

[1] And other irregularities such as for instance the variability of the ratio of sulphur to copper in ppd. sulphide of copper.

[2] We will avail ourselves of this opportunity for referring to the process of fractional filtration as useful in

To pass to another example. There is a series of reducing agents R, the solutions of which, when mixed with a solution of iodine in iodide of potassium, are oxidised into products R′, while the corresponding quantity of free iodine passes into iodide.

For example:—

$$\left.\begin{array}{ll}\text{I.} & SO_2+H_2O+I_2=2HI+SO_3\\ \text{II.} & 2S_2O_3R_2+I_2=2RI+S_4O_6R_2\\ \text{III} & As_2O_3+2H_2O+2I_2=4HI+As_2O_5\\ \text{IV.} & Sb_2O_3+2H_2O+2I_2=4HI+Sb_2O_5\\ \text{V.} & SnCl_2+2HCl+I_2=2HI+SnCl_4\end{array}\right\}\text{ in solution.}$$

Each of these reactions takes its normal course only under certain conditions, which, however, in cases I. to IV. at least, are easily established. All go on readily in the cold; and with all, starch solution is a safe and delicate indicator of excess of free iodine. Hence, to determine any of our reducers, R, we bring it into solution in the proper manner, add starch solution, and then drop in iodine solution from the burette until the blue colour of iodide of starch, which appears locally from the first, becomes permanent on stirring. Supposing t c.c. of iodine solution to have been used, and one c.c. of it to contain $\tau \times 127$ mgms. of free iodine, the weight of R is $t\tau$ ($\frac{1}{2}SO_2$, S_2O_3, $\frac{1}{4}As_2O_3$, $\frac{1}{4}Sb_2O_3$, $\frac{1}{2}SnCl_2$), as the case may be. By theory, any one of our reducers might serve as a reagent for the measurement of free iodine; in practice sulphurous acid and alkaline thiosulphate work best.

According to Bunsen, sulphurous acid acts normally on iodine, if it is diffused through at least 3,000 times its weight of (air-free) water. For the determination of free iodine he uses an aqueous sulphurous acid diluted to the extent stated, in combination with a standardised solution of iodine. The sulphurous acid is measured out by means of a glass-stoppered cylinder (or a narrow necked flask with one mark on the neck) holding some 100-200 c.c. To determine an unknown weight (x mgms.) of free iodine given as solution in HI or KI solution, we add the least number n of measures of the sulphurous acid water which suffices to decolourise the solution, then starch solution, and lastly, from the burette, standard iodine, until the blue colour becomes permanent after addition of, let us say, t c.c. On the other hand, we ascertain the number, t_0, of c.c.s of standard iodine required for 1 measure-full of the sulphurous acid. Obviously, $nt_0\tau \times 127 = x + t\tau \times 127$ (mgms. of I_2). Whence $x = (nt_0 - t)\ \tau \times 127$.

So far Bunsen had done no more than translate an old process for determining SO_2 into a precise method for determining iodine. His great merit was to see that, given a method for determining free iodine, we have an indirect method for the determination of any of the large number of oxidising agents for which a definite proportion of iodine can be substituted by the purely qualitative execution of suitable reactions.

cases like that referred to. Instead of filtering off the CuO pp., we allow the mixture to cool, dilute to a known volume, v c.c., filter through a *dry* filter, and measure off a known aliquot part of the filtrate, v c.c., for the titration. If v is sufficiently large, the volume of the CuO need not be taken into account; supposing for instance v=500 c.c. and the pp. of CuO amounts to 1 gm., the error introduced by neglecting its volume amounts certainly to no more than about 0·5 c.c., or 0·001 of the whole.

Thus, for instance, we may determine free bromine, iodate RIO_3, bromate $RBrO_3$, hypochlorite RClO, ozone O_3, by letting the respective substance act on excess of iodide of potassium solution, acidifying with hydrochloric acid, and then titrating the iodine liberated as above explained.

From the respective equations, we see that Br_2, or Cl_2, or RClO, or O_3, liberates I_2; and that RIO_3 or $RBrO_3$ liberates $3I_2$.

The same principle obviously applies to all those peroxides which, when distilled with excess of hydrochloric acid, liberate a definite proportion of chlorine. As examples: $MnO.O_x$ (when distilled with HCl) yields $x \times Cl_2$ of free chlorine, which when passed into iodide of potassium solution liberates $x \times I_2$ of iodine. Hence for every one I mgm. obtained, there was $\frac{1}{2x} \times (MnO.O_x)$ mgms. of *that* peroxide of manganese. And similarly (to quote another case which is known to work) every CrO_3 mgm. of chromic trioxide, liberating $3 \times Cl$, ultimately yields $3 \times I$ mgms. of iodine; or, in this case, every $1 \times I$ mgms. corresponds to $\frac{1}{3}CrO_3$, or to $\frac{1}{6} \times K_2Cr_2O_7$ if the CrO_3 was present in this form. It is as well to mention that what the method in any case really determines is, not the respective species, but the I_2-yielding radicle; the active oxygen in the $MnO.O_x$, or the $Cr_2O_3.O_3$, or RClO; the O_3 in the KIO_3; the *one* O in O_3, &c.

The applicability of the general method, however, goes further. As ferrous chloride is readily converted into ferric salt by free chlorine, we can determine an unknown weight of *ferrosum* (ferrous iron) (given as $FeCl_2$, FeO, $FeSO_4$, &c.) by distilling the respective substance with a weighed excess of potassium dichromate and hydrochloric acid, and collecting the chlorine in iodide of potassium, &c. Supposing we used $k \times K_2Cr_2O_7$ mgms. of this salt, the chlorine furnished by it is $6 \times k \times Cl$ mgms., and, if the iodine obtained at the end was $(nt_0 - t) \times \tau \times I$ mgms., then $6k \times Cl - (nt_0 - t)\tau Cl$ must have been used by the $FeCl_2$, and consequently, $\{6k - (nt_0 - t)\tau\} \times (Fe = 56$ mgms.) of ferrosum must have been present in the substance analysed.

Strictly speaking, all volumetric methods are empirical methods, in this sense, that the fundamental chemical equation is only an approximate theory of the process. Hence, unless we are sure that the error in the equation, considered as a theory of titration, is less than the unavoidable error involved in the operations, to attain the highest possible degree of precision we must standardise our measuring reagent (if possible) by means of a known weight of the very thing (or radicle) to be determined, and both in the standardisation and the analyses we must maintain as nearly as possible the same conditions. To illustrate this, let us assume we had to analyse a series of alkaline carbonates by means of a standard hydrochloric acid. Ppn. of a known volume of the reagent by nitrate of silver, and weighing the pp. of AgCl (or the corresponding process of titration) would no doubt give the most exact result for the number of mgms. of HCl contained in 1 c.c. of the reagent. Yet it is better in our case to standardise the

acid by means of a known weight of pure carbonate of soda, although this method, as one for the determination of HCl, could not for a moment be compared with either silver process in point of inherent precision.

In now passing from generalities to the consideration of individual methods, we shall confine ourselves in the main to those methods which are applicable to whole classes of bodies. Under the head of each we shall briefly state what applies to it as a *general* method. For special applications of these methods, as for special methods generally, also in regard to technicalities, we must refer to the special handbooks.[1]

I. *Methods based on double decompositions.*

Theoretically these processes are founded on equations of the form

$$\underset{A,}{ax} + \underset{B,}{by} = \underset{C,}{ab} + \underset{D,}{xy}$$

where a and b are the constant radicles characteristic of the process. Here we have to distinguish between two cases:—I. *C and D remain dissolved.* Only a very few processes fall into this group. As an example, we may quote Liebig's process for the titration of NCH by neutral nitrate of silver. Large excess of potash is added, the liquid is diluted largely, and, after addition of a little NaCl as indicator, standard $AgNO_3$ (neutral) is dropped in until the cloud of AgCl becomes permanent, showing that the reaction $2KNC + AgNO_3 = KAg(NC)_2 + KNO_3$, has been just completed. II. *The characteristic product C = ab comes down as a pp.* Of these numerous processes, only those need now be noticed in which, on account of the absence of an *end-reaction*, and of a suitable indicator, the end-point cannot be recognised otherwise than by proving quite directly that the ppn. has just reached its end. If the pp. settles readily, this can be done with comparative ease—in an obvious manner; but easily settling pps. are exceptional. It is more generally practicable to get the pp. to settle so far that it is possible to draw off a few drops of the clear top-stratum, and to examine them on a watch-glass by addition of a drop of B, or of a solution of A, or of any delicate reagent for A or B. If this method does not work, the only course left is, from time to time, to take out a little of the mixture, filter it through paper, and examine the filtrate. One way of doing this is to put a drop of the fluid on a small double filter-paper, and to examine the lower filter by means of some reagent which strikes an intense colour with A or B as the case may be. But such colour-tests are not always available, so that ordinary filtration must generally be resorted to. Each such filtration of course means a loss of a, and consequently ought to be done with a measured aliquot part of the whole, to enable one to allow for the loss by calculation. This, however, is apt to lead to errors; in practice it is better in the first trial to neglect the error, and in a second and third practically to avoid it by filtering only a few times near the end of the process, when the amount of unppd. A has become very small. In any case it is convenient to have a standard solution of some reagent, ax', by means of which to retrace one's steps if an excess of pptnt. has been added. This auxiliary solution is best adjusted so that it pps. exactly its own volume of D. The method of procedure then assumes this form:—We add B, finally in small instalments of, say, 4 c.c. each, until by the last instalment the end-point has been over-stepped; we then go back with A-solution, adding it in instalments of 2 c.c., until *this* reagent is in excess; we then again apply B in portions of 1 c.c., &c., until we come to know that, say, v c.c. of B is too little, while v + 0·2 c.c. is an excess; or that (v + 0·1 c.c.) ± 0·1 c.c. may be adopted as the final result.

Of the vast number of *precipitation-analyses* which have been invented, only those founded upon mutual decomposition of solutions of Silver salts and haloids occupy the rank of precise methods. If (dissolved) chloride and (dissolved) silver-salt meet in a neutral or acid solution the whole of the potential chloride of silver is formed, and comes down as a pp. as demanded by the equation,

$$RCl + AgNO_3 = AgCl + RNO_3.$$

Upon this, and the fact that the AgCl (if sufficiently abundant) readily unites on shaking into a quickly settling pp., Gay-Lussac long ago founded his famous process for the determination of silver by standard NaCl solution, which process is directly translatable into an equally exact process for the determination of chloride by standard silver. The equation, however, is not an absolutely correct theory of either process. Gay-Lussac observed that if the silver nitrate and the sodium chloride are exactly balanced against each other, the clarified mixture gives a distinct cloud with either reagent. Hence to exactly complete the ppn. of (say) $AgNO_3$ mgms. by salt, we must add, not NaCl, but a trifle more, call it $(1 + \alpha)$NaCl mgms. And similarly, the complete ppn. of NaCl mgms. demands $(1 + \beta)AgNO_3$ mgms. The exact values of α and β vary with the experimental conditions, and are not susceptible of separate determination. Hence to determine an unknown weight, $x \times$ Ag mgms. of silver (if we do not care to neglect the correcting factors), all we can do is: (1) to add standard chloride solution—at last in very small instalments, corresponding to say 0·02 mgms. of silver each—until the ppn. is exactly completed by, say, $n \times$ RCl mgms. as calculated from the strength of the solution, and the quantity used. We then (2) titrate back with (very dilute) standard silver until the last drop no longer gives a cloud of AgCl, which will take, say, $\epsilon \times$ Ag mgms. The mixture now is (practically) in the same condition as if no silver had been added but the chloride diminished by $\epsilon \times$ RCl mgms.

Obviously the truth lies between $x = n$ and $x = n - \epsilon$, and we may say $x = \left(n - \frac{\epsilon}{2}\right) \pm \frac{\epsilon}{2}$.

Or, to put it somewhat differently; we have

$2x = 2n + (\beta - \alpha)n - \epsilon$ . . . . . . I.

and $0 = n(\beta + \alpha) - \epsilon$ . . . . II.

If we knew that $\alpha = \beta$, we should have $x = n - \frac{\epsilon}{2}$ exactly.

[1] Mohr's *Lehrbuch der chemische-analytischen Titrirmethode*; 2, Fleischer, *Die Titrirmethode*; 3, Fleischer, *Die Titrirmethode*, English edition *Volumetric Analysis*, translated by M. M. Pattison Muir; 4, Sutton, *Volumetric Analysis*; 5, Fresenius, *Quantitative Analysis*.

According to Mulder, if the silver, calculated as metal, amounts to about 1 gram, and is diffused throughout some 120 to 150 c.c. of mixture $(\alpha+\beta)=0{\cdot}001$, about.[1] The explanation given in regard to chlorides holds substantially for bromides, iodides, cyanides (NCR); sulphocyanides (perhaps also for cobaltocyanides, and some other metallo-cyanides); in the case of bromides, however, the numbers α and β are practically equal to *nil* (Stas), AgBr being even more insoluble in HNO_3 and KNO_3 &c. solutions than AgCl is; hence we may *surmise* that the $(\alpha+\beta)$ for iodide is still nearer to nothing. The cases of NC.R and NCS.R have not been investigated in this sense. Presumably the $(\alpha+\beta)$ for cyanide is greater than, and that for (NCS)R is about equal to, the value for chlorides.

Given (let us say) an alloy for which the percentage of silver is approximately known (say to $\pm 0{\cdot}5$ p.c.); the exact determination of the noble metal by titration with standard chloride (*e.g.* NaCl) solution offers no difficulty; but with an alloy &c. of utterly unknown composition the process even in practised hands is apt to be tedious. Practical assayers, indeed, never apply Gay-Lussac's method without having first made a preliminary assay by the old method of cupellation. Volhard, some years ago, invented a modification of Gay-Lussac's method, which, with a small number of samples at least, is quicker even than cupellation, and, in all cases, is more accurate. He dissolves a known weight (equal to presumably 0·5 grm. of silver) in nitric acid, dilutes moderately, *boils off all the* N_2O_3, adds 5 c.c. of saturated iron-alum solution, and then drops in standard sulphocyanide of potassium (or ammonium) until the red colour of $Fe(NCS)_3$ becomes permanent. (The large quantity of indicator prescribed is necessary, or else the end-reaction lacks delicacy.) For the determination of chlorine (given as RCl), Volhard pps. the chlorine first by an excess of standard silver, he then adds iron-alum, and (without removing the AgCl[2]) titrates back with KNCSAq until the end-point is reached.

A very handy (but less exact and less widely applicable) method, introduced by Mohr, may here be referred to. He brings the chloride into neutral or very feebly alkaline solution, and, after adding a few drops of yellow chromate of potassium, titrates with neutral silver nitrate until the red colour of the Ag_2CrO_4 becomes permanent. The method, if used as an empirical one, gives very good results.

STANDARD SUBSTANCES AND SOLUTIONS.

1. *Standard silver.*—Best prepared by Stas's[3] process (precipitation of a cupriferous ammoniacal solution of nitrate by added alkaline ammonium sulphite). The ppd. metal, after having been washed, first with ammonia in the presence of air, then with water, is heated to redness, when it becomes semi-compact. It is then broken up in a mortar into granules, again heated, and preserved in this form. There is no need of going to the trouble of fusing the metal, provided it is proved to be free from every trace of chloride.

2. *Standard chloride.*—Pure chloride of sodium is universally recommended. The writer prefers pure KCl prepared by strongly heating re-crystallised perchlorate. The perchlorate is deoxygenated as far as convenient in a platinum basin, and then fully by fusion in a platinum crucible. The fused salt is quite neutral; yet for *very* precise work it is perhaps better to dissolve the fused salt in water, add hydrochloric acid, evaporate to dryness (in platinum), and keep the residue at a temperature just short of the fusing point until the weight is constant.

3. *Standard solutions of* 1 *and* 2.—Both can be standardised synthetically, on the basis of Stas' atomic weights; for general purposes $\frac{Ag}{10}$ and $\frac{KCl}{10}$ grms. per litre are convenient strengths. For exact work the solutions are combined with centinormal solutions, containing $\frac{Ag}{100}$ and $\frac{KCl}{100}$ grms. per litre.

4. *Pure bromide of potassium*, and standard solution ($\frac{KBr}{10}$ grms. per litre) of the same for *very* precise determinations of silver. Regarding the preparation of the pure salt, see Stas's *Memoir*.

5. *Standard sulphocyanide.*—About $\frac{1}{10}$ $NCS.NH_4$ grms. of the pure (chlorine-free) ammonium salt is dissolved to 1 litre, and the exact strength is determined empirically by means of a known weight of silver dissolved as nitrate.

II. *Methods based on saturations*, that is, reactions of the type

$$XH + ROH = HOH + XR;$$

regarding these, we have little to add to what was given under *Theory of Titration* (*q.v.*). For $XH = NO_3H, \frac{1}{2}SO_4H_2, ClH, HClO_4$, and other strong acids (including oxalic and formic) on the one hand, and $R = K, Na$, generally, and for $R = \frac{1}{2}$ (Ba, Sr, Ca) as long as no insoluble salt is produced, on the other, the equation is a strictly correct theory of the process. For phosphoric acid, HX must be taken as representing $\frac{1}{2}H_2(HPO_4)$, RHO being an alkali, but even then the results are not very constant. For weaker acids, such as acetic, butyric, &c., the method is purely empirical. An approximation to a standard acetic acid is obtained by measuring off a known volume of standard sulphuric acid, and adding say two equivalents of perfectly neutral acetate of soda. In determinations of ammonia it is as well not to assume that NH_4OH is an absolutely exact equivalent for KOH or NaOH.

STANDARD SUBSTANCES AND SOLUTIONS.

1. *Pure carbonate of sodium*, as a general standard alkali. Prepared from pure bicarbonate (recrystallised as such) by strongly heating in platinum. The salt must not be fused for de-

[1] Our impression is that Mulder over-estimated the value.

[2] The writer finds that high precision can be reached only by *removing* the AgCl pp. before titrating back with KNCS. (See Dittmar's *Report on the Composition of Ocean Water*, p. 4. ['Challenger' Memoirs.] Also his *Exercises in Quantitative Analysis*, section on *Sea-water*.)

[3] *Recherches sur les rapports réciproques des poids atomiques* (Bruxelles, 1860); and *Nouvelles Recherches*, &c. (Bruxelles, 1865), or German translation of both works Aronstein (Leipzig, 1867).

hydration, or else it loses carbonic acid. To obtain a really pure, and especially a potash-free, salt, the best method is to add pure oxalic acid to a decided excess of solution of the purest obtainable carbonate of soda, to collect the pp. of $C_2O_4Na_2$ formed, to wash it by displacement and to reduce it to Na_2CO_3 by heating strongly (W. D.).

2. *Oxalic acid*, $C_2H_2O_4 + 2H_2O$, recommended by Mohr as a general standard acid. See that the preparation is free from fixed matter (*e.g.* potassium salts). If not, recrystallise it from hot 10 p.c. HCl, repeatedly, and lastly from water (Stolba). The carefully air-dried crystals have the correct composition. We prefer a hydrochloric acid, standardised by silver, for general purposes.

3. *Solution of standard acid.*—Sulphuric works best for alkalis; hydrochloric is preferable for general purposes. The latter may be standardised by means of silver; either acid by means of a known weight of carbonate of soda,[1] with standard alkali as an auxiliary reagent. Thorpe recommends for the standardisation of SO_4H_2, to add a known (excessive) weight of Na_2CO_3, to evaporate to dryness, heat, and weigh the residue. As every Na_2CO_3 grms. in passing into Na_2SO_4, gains $(SO_4 - CO_3)$ grms., every 1 grm. of gain of weight corresponds to $\frac{SO_3}{SO_4 - CO_3}$ grms. of sulphuric anhydride. (I have tested this method, and found it to give very good results.—W. D.)

4. *Solution of standard alkali.*—Caustic potash or caustic soda for general purposes. The reagent must be as free as possible from carbonate. The preparation known as *potash purified by alcohol* almost fulfils this condition. The best method is to causticise an almost carbonic acid free (dilute) ley with a *slight* excess of baryta in a nickel vessel; allow to settle, and preserve in a bottle provided with a protection-tube filled with granulated soda-lime, or baryta, $Ba(OH)_2$. The trace of dissolved BaO disposes of traces of CO_2 that find their way into the reagent while being preserved. $\frac{1}{2}$ROH grms. per litre is a convenient strength. It is standardised empirically against measured standard acid.

5. *Standard baryta water* containing about $\frac{1}{8}Ba(OH)_2$ grms. per litre is used for special purposes, *e.g.* determination of free or liberated CO_2. A stronger reagent is apt to deposit crystals in cold weather. It is standardised empirically against standard hydrochloric acid. In the absence of sulphates, baryta water is the best standard alkali for all purposes.

III. *Methods based upon processes of oxidation and reduction.*

(As illustrated in *Theory of Titration*, by reference to Bunsen's methods.)

I. Iodine (solution of I in KI) as oxidant is available for the measurement of the following reducers:—

1. *Dissolved sulphurous acid* acts normally under the conditions stated under *Theory of Titration*.

2. *Dissolved alkali thiosulphate* (in the absence of excess of alkali; even carbonate is not permissible) acts normally at any state of concentration which one could reasonably employ. In the *presence of acid* the reaction takes its normal course only if the solution is sufficiently diluted, and the $H_2S_2O_3$ has no time to decompose spontaneously. In practice, however, this spontaneous decomposition is out of court, because, in all cases in which free acid is present, it forms part of the iodine solution, and the thiosulphate plays the part of reagent, so that the $S_2O_3H_2$ liberated passes at once into $S_4O_6H_2$, which is sufficiently stable. Free sulphuric acid in any quantity must be avoided (*v. supra*); free hydrochloric acid in moderate quantity does no harm, if the given iodine solution is diluted to about $\frac{1}{4}$–$\frac{1}{5}$ of the strength of the customary standard solution.

3. *Alkaline arsenite.* The reaction proceeds (not as promptly as those of 1 and 2, but) in a fair degree normally, provided there is enough of *pure* carbonate or bicarbonate of alkali to keep up an alkaline reaction to the end (Mohr). The best auxiliary alkali to add is sesqui-carbonate of ammonia; it does not decolourise iodide of starch, to anything like the (slight) extent to which Na_2CO_3 does (Mohr; later communication).

4. *Alkaline antimonite*, or rather Sb_2O_3 given as tartar emetic or in similar forms, is oxidised by iodine just as As_2O_3 is (Mohr). Results fair.

5. *Stannous chloride.* The execution of the process $(SnCl_2 + 2HCl + I_2 = 2HI + SnCl_4)$ offers no difficulty, and added starch solution defines the end-point sharply; but the results are very variable and inexact.

6. *Sulphuretted hydrogen H_2S* (in *much* air-free water) with iodine reacts substantially thus:—$I_2 + H_2S = 2HI + S$. Results are only approximate, yet the method is of some value for determining *small* quantities of H_2S in much water.

II. Iodine in combination with reducers for general purposes.

Only the combinations I_2 and H_2SO_3, and I_2 and $Na_2S_2O_3$ are used now-a-days. Discussion anticipated in section on *Theory of Titration*.

III. Permanganate of potassium, as an oxidant,

measures the following reducers directly, and in all cases the intense colour of the reagent marks the end-point with great sharpness.

1. *Ferrosum.* A dilute, strongly acid, solution of ferrous sulphate, when titrated with solution of permanganate, is promptly oxidised into ferric salt with formation of MnO-salt from the reagent (Marguerite).

Conditions of success:—*a*, large dilution; 1 litre of solution should contain at most 1 gram of metallic iron; *b*, a sufficiency of free sulphuric acid, more than the equation demands, or else MnO_2 may separate out as a pp.; *c*, absence of hydrochloric acid (and chlorides generally), or else part of the reagent is reduced by it with formation of Cl_2. According to Zimmerman, however, this by-reaction can be prevented by addition of manganous sulphate to the ferrosum solution. 4 grams of the salt $MnSO_4 + 4H_2O$,

[1] Ppn. with $BaCl_2$ and weighing the $BaSO_4$ is not a very exact method for the standardisation of a sulphuric acid.

suffice per 60 c.c. of 20 p.c. HCl used for dissolving the respective iron compound.

Iron given as ferric salt may be reduced to ferrous salt, by (1) treatment with H_2S; (2) prolonged treatment in a warm solution with Na_2SO_3 and HCl (works better with chloride than with sulphate solution)—in either case the excess of reducer must of course be expelled by ebullition —(3) zinc and acid; handy, but not so trustworthy as (1) or (2).

2. *Oxalic acid.* A strongly sulphuric solution of this acid is oxidised by the reagent into carbon dioxide and water (Hempel). The reaction at first proceeds very sluggishly, but then more and more promptly, as the quantity of $MnSO_4$ produced increases. Hence the expediency of adding $MnSO_4$ from the first (De Koninck). Whether hydrochloric acid interferes with this reaction as with the preceding one (whether, for instance, it is permissible to dissolve oxalate of lime given for the determination of its oxalic acid in hydrochloric acid before titrating) has not yet been determined.

3. *Arsenious acid.* Arsenious acid in strongly hydrochloric solutions is oxidised by permanganate into arsenic acid, but part of the manganese separates out as MnO_2 (Kessler).

4. *Antimonious acid* as $SbCl_3$, in a solution which contains not less than 1-2 volumes of hydrochloric acid for 5 of water, is readily and completely oxidised into Sb_2O_5. The reaction is available quantitatively. [(3) and (4), Kessler, *J.* 1863. 683)].

5. *Sulphurous acid* is readily oxidised into sulphuric; not investigated quantitatively, as far as we know.

6. *Peroxide of hydrogen.* In the presence of water and dilute sulphuric acid, the mutual reduction

$$5H_2O.O + Mn_2O_7 = 5H_2O + 2MnO + 5O_2$$

proceeds normally and promptly.

7. *Nitrous acid* (liberated from nitrite by H_2SO_4 in *very* dilute solutions) is oxidised by permanganate to nitric acid. Results, under certain conditions, fair.

8. *Cu_2O* (ppd.) dissolved in acid iron alum, is oxidised readily, and fairly normally, to 2CuO.

IV. Combined application of permanganate and reducing agents.

A. Ferrosum as reducer.

The higher oxides of manganese, when digested with HCl or dilute H_2SO_4 and excess of ferrous salt, are readily dissolved as MnO-salt, with formation of a quantity of ferricum proportional to the loosely held oxygen in the peroxide. In the absence of atmospheric oxygen, *i.e.* in an atmosphere of CO_2, the reaction takes its normal course, and becomes available for an obvious remainder-method for the determination of such oxygen. No doubt available for other peroxides.

Upon the ready action of *alkaline* permanganate on the sulphides, sulphites, thiosulphates, iodides, arsenites, formates, of K or Na, with formation of sulphate, iodate, arsenate, carbonate, respectively (and hydrated binoxide of manganese), Péan de St. Gilles (*A. Ch.* [3] 55, 374), has founded a general method for the determination of the respective acids by means of a standard solution of permanganate, and an auxiliary solution of ferrous sulphate. After having carried out the required oxidation by means of excess of permanganate and a sufficiency of caustic potash, the mixture is acidified, the MnO_2 and surplus Mn_2O_7 reduced by addition of, first, acid, and then excess of ferrous solution, and finally the surplus ferrosum is titrated by addition of more of the permanganate solution.

B. Oxalic Acid as reducer.

Any higher oxide of manganese, $MnO.O_x$, when digested with excess of oxalic acid and sulphuric acid, is dissolved as $MnSO_4$, with formation of CO_2 from the reagent. The oxalic acid is used as a standard solution, and what remains over after the oxidation is determined volumetrically by permanganate. (Calcium oxalate may separate out as a pp.)

V. Chromic acid (in practice a solution of $K_2Cr_2O_7$) as oxidant

is available for the direct titration of the following reducers:

1. *Ferrosum.* Ferrous sulphate or chloride, in the presence of free acid, is readily and completely oxidised by added bichromate solution. The latter may be standardised synthetically (or analytically by means of a known weight of dissolved ferrosum). The end point is recognised by means of ferricyanide as a *drop-test.* The results are in exact accordance with the chemical equation, even in the case of hydrochloric solutions (Penny; Schabus). An unknown weight of CrO_3 can be determined with equal exactitude by adding a known excessive weight of ferrosum (as sulphate) to the previously acidified solution, and titrating back with bichromate solution.

The combination *$K_2Cr_2O_7$ and ferrous salt* is equivalent to that of $Mn_2O_7K_2O$ and the same reducer. It is available likewise for the determination of As_2O_3 and Sb_2O_3 in strongly hydrochloric solutions. The solution is mixed with a (measured) excess of bichromate solution, and the mixture allowed to stand to give the oxidation time for completion; a known excessive quantity of ferrosum is then added, and its excess is titrated by means of bichromate (Kessler).

2. *Sulphurous acid, Sulphuretted hydrogen, Stannous chloride,* in mineral acid solutions, are readily oxidised by CrO_3 into SO_3, $S + H_2O$, $SnCl_4$, respectively, and in all cases iodide of potassium and starch afford a sensitive indicator of excess of oxidant, which sharply defines the apparent end-point of the process. But, unfortunately, the corresponding ratio of the reagents in no case coincides with that demanded by the respective equations, nor is it even constant in itself. It varies according to the degree of dilution, the proportion of free acid, the quantity of absorbed air in the reagents, &c., in a manner which defies all calculation (Kessler, Mohr, Casselman).

VI. Ferric chloride, in combination with Stannous chloride.

The oxidation of an acid solution of $SnCl_2$ by added ferric chloride proceeds very readily when the liquid is hot, and in fair accordance with the equation:

$$SnCl_2 + Fe_2Cl_6 = SnCl_4 + 2FeCl_2;$$

but the dissolved air of the reagents is drawn

into the oxidation, and the results are consequently irregular. If however (according to Fresenius) we start with a hot, strongly acid, solution of ferric chloride, and at a nearly boiling temperature drop in stannous chloride, the process proceeds exactly as described by the equation, and the disappearance of the last trace of the yellow colour of the ferric salt defines the end-point very sharply. In case of doubt, add a slight excess of $SnCl_2$, *allow to cool*, add starch, and titrate with iodine solution to determine the excess of $SnCl_2$, and allow for it. According to the writer's experience the whole of these operations must be done in an atmosphere of CO_2, else the results are not exact. Fresenius utilises the process for the determination of nitric acid. The nitrate to be analysed is allowed to react with an excess of ferrous sulphate, strongly *acidified by HCl*, in an atmosphere of H or CO_2 first cold, then hot; the NO is boiled off, and the ferricum produced is determined by means of standard $SnCl_2$. The ferricum present as an impurity in the ferrous salt is determined by a blank experiment, and is allowed for: $6 \times Fe$ of ferricum produced, indicate $1 \times N_2O_5$ of nitric anhydride.

STANDARD SUBSTANCES AND SOLUTIONS, FOR THE PROCESSES OF OXIDATION REFERRED TO.

1. *Pure iodine* is best made by Stas's method. Ordinary iodine is dissolved in the minimum of a highly concentrated solution of iodide of potassium, and re-ppd. as far as possible by dilution with water. The pp. is washed, dried first on a porous tile, then over CaN_2O_6. The dry product is distilled (or the small quantity needed for an experiment sublimed *ex tempore* between watch-glasses), the first instalments of vapour being rejected on account of possible contamination with water. From such iodine

2. *A standard iodine solution* might easily be made by exact synthesis. But it is more economical and less troublesome to prepare this solution by approximate synthesis from ordinary good iodine (5 grams of I_2 dissolved in 10 grams of IK and 10-20 c.c. of water in a mortar, and diluted to 1 litre, gives a solution of convenient strength); and to determine the exact strength by comparison with a known weight of pure iodine, by means of a thiosulphate solution of arbitrary strength. Supposing p mgms. of pure iodine weighed directly, and dissolved in IK solution, require t_0 c.c. of thiosulphate for their decolourisation, while n c.c. of the iodine-solution require t c.c.; then 1 c.c. of thiosulphate is equivalent on the one hand to $\frac{p}{t_0}$ mgms. of iodine, and on the other to $\frac{n}{t}$ c.c. of iodine-solution. Hence 1 c.c. of the latter contains $\left(\frac{pt}{t_0 n \times 127}\right) \times I(=127)$ mgms. of pure iodine.

3. *Thiosulphate solution.* — Made by dissolving 10 grms. of the pure salt, $Na_2S_2O_3.5H_2O$, in water, to 1 litre. It decolourises about its own volume of the above iodine-solution. The strength is determined empirically by means of the latter.

4. *Arsenious acid.*—Pure As_2O_3 is to be had in commerce; but the best qualities even are liable to be contaminated with Sb_2O_3. powder is not hygroscopic.

5. *Arsenite solution.*—4·95 grms. = $\frac{As_2O_3}{40}$ powdered As_2O_3 along with 11 grms. of p Na_2CO_3 (= 30 grms. of crystals, $Na_2CO_3 + 10H$ are dissolved in a slanting litre flask in wat over a water-bath; after cooling, the liquid diluted to 1 litre. 1 c.c. = 0·1 × 'I,' 'Cl,' d mgms. [This solution, as a reagent, may ser for the direct titration of dissolved hyp chlorite — $2RClO + As_2O_3 = 2RCl + As_2O_5$. Th end-point is recognised by means of iodide potassium and starch paper; a drop of th mixture when placed on the paper produces blue stain only as long as the RClO is in exces (Pénot)].

6. *Standard ferrosum.*—Fine pianoforte wir is sure not to contain more than 0·4 p.c. c impurities, and consequently may be assume to represent 0·998 ± 0·002 times its weight o real iron. A known weight is dissolved in HC or dilute H_2SO_4, in the absence of air, &c. More convenient is

Ferrous sulphate.—$FeSO_4.7H_2O$, ppd. from a pure, hot, concentrated, acid solution, by alcohol. The ppd. salt is washed with alcohol, dried on bibulous paper, and finally by exposure to the 'dry' air of a room. The dried salt is sifted to remove lumps, again exposed to the air for a while, and bottled up for use. The exact percentage of iron is determined by strongly heating a known weight in a platinum crucible—at the end in the presence of air—until the weight is constant, and weighing the Fe_2O_3. This old preparation of Otto, according to the writer's experience, has a higher degree of stability in air than Mohr's salt $(Fe(NH_4)_2S_2O_8.6H_2O)$.

7. *Standard oxalic acid.*—The crystallised, normal, ammonium salt is the best standard oxalate for processes in which it serves as a reducing agent. If air-dry, it has exactly the composition $C_2O_4(NH_4)_2 + H_2O = 142$.

8. *Standard permanganate of potassium.*—An almost pure salt is to be had in commerce. Yet it is not pure enough to serve as a standard substance in itself. A convenient solution is obtained by dissolving a little more than 3·16 grms. (= 5·6 grms. of ferrosum) in water, in a mortar, and diluting to 1 litre. The solution is standardised by means of a known weight of ferrosum or oxalate of ammonium, according to the object which it is meant to serve.

9. *Bichromate of potassium.*—$K_2Cr_2O_7$. The pure salt is not difficult to obtain; but it is not easy to prove that it contains exactly $2CrO_3$ for $1K_2O$. Besides, the uncertainty of the atomic weight of chromium is a difficulty. To prepare the salt for use, it is powdered and dehydrated by keeping it near its fusing-point for a time in a platinum basin. It is then fused at the lowest temperature, and allowed to solidify, when it breaks up spontaneously into small granular fragments, and thus assumes a convenient form for weighing.

10. *Standard solution of bichromate of potassium.*—A convenient concentration is $\frac{K_2Cr_2O_7}{60}$ = 4·92 gms. per litre. It may be standardised

synthetically; but for the reasons stated it is on the whole preferable to standardise the solution analytically by means of a known weight of dissolved ferrosum.

11. *Standard ferric chloride.*—Pure ferric oxide is prepared by strongly heating ferrous oxalate. It is dissolved, by prolonged digestion, in fuming HCl, and the solution is diluted to the right volume. $\frac{Fe_2O_3}{20}$ = 8 grms. per litre is a convenient strength.

12. *Stannous chloride* (for No. 11). Pure granulated tin (approximately weighed) is boiled with pure HCl until a sufficiency of the metal is dissolved. The residual metal is weighed, to ascertain how much has passed into solution. For every 3 grms. of dissolved tin, the solution is diluted—with air-free water—to 1 litre. The solution decolorises about $\frac{1}{3}$ its volume of the iron solution, which latter serves for its standardisation. This solution is so prone to oxidise in the air that it must be restandardised expressly for each analysis. W. D.

ANALYSIS, ORGANIC. Ultimate organic analysis is the determination of the elements present in an organic substance. Proximate organic analysis is the determination of the compounds present in a mixture, or of the radicles present in a compound.

ULTIMATE ANALYSIS.

Qualitative.

Carbon. If a substance blackens when it is heated either alone or with sulphuric acid it probably contains carbon, in which case the black residue may be burnt away by heating to redness in air. A substance that does not blacken may nevertheless contain carbon. A more general method of detecting carbon is first to warm the substance gently with dilute sulphuric acid, in order to expel CO_2 that may be present as carbonate, and then to add several volumes of strong H_2SO_4 and some $K_2Cr_2O_7$; when the mixture is heated any organic substance will be oxidised, and the escaping CO_2 will give a pp. with lime-water.

Hydrogen. The substance is mixed in a tube with dry CuO or $PbCrO_4$ and heated to redness; water comes off and condenses in a cold tube. Very small quantities of water may be detected by passing the gases through a glass tube lined with P_2O_5, which will deliquesce. In these experiments carbon may be detected by passing the escaping gases into lime-water.

Nitrogen. The substance is heated with soda-lime and the nitrogen may then be given off as NH_3 and detected by its smell, action on red litmus, or fumes with HCl. The soda-lime must be strongly heated before use, until it no longer gives off NH_3. This test will not succeed with compounds rich in oxygen. A more delicate test consists in heating the substance with potassium in a test-tube drawn out to a point. After deflagration, the mass is dissolved in water and examined for cyanide (Lassaigne, *A.* 48, 367). This test is not applicable to diazo-compounds (Graebe, *B.* 17, 1178).

Chlorine. The chlorine is eliminated in the form of a chloride, the presence of which is detected by $AgNO_3$. The conversion into chloride can be effected: (*a*) by boiling with fuming HNO_3; in the case of volatile substances, the operation must be performed in a sealed tube: (*b*) by boiling with alcoholic potash: (*c*) by mixing with quicklime and heating to redness: (*d*) by heating with H_2SO_4 and MnO_2.

Bromine and *iodine* may be detected by the same methods.

Halogens may also be detected by fixing a lump of CuO to a platinum wire, dipping it into the substance, and heating first in the inner and then in the outer part of a Bunsen flame: a green colour indicates halogens (Beilstein, *B.* 5, 620).

Sulphur is detected by strongly heating the substance with a mixture of sodic carbonate and sodic nitrate, or sodic carbonate and potassic chlorate; and testing the product for sulphate. Or the substance may be fused with sodium free from sulphur in a test-tube, and the product examined for sulphide (Schönn, *Fr.* 8, 52, 399). Some compounds, such as albumen, give a black pp. of PbS when boiled with a solution of PbO in NaOHAq. Boiling $HgCl_2$ or ammoniacal $AgNO_3$ often give a black pp. of metallic sulphide.

Phosphorus may be detected by fusing with Na_2CO_3 mixed with $NaNO_3$, and examining the product for phosphate. Or the carbonised substance may be heated with magnesium powder; the product, containing magnesium phosphide, is luminous in the dark, and when moistened with water will give off PH_3 (Schönn, *Fr.* 8, 55).

Quantitative.

Substances containing no elements beside carbon, hydrogen, and oxygen.

The substances are subjected to *Combustion* as proposed by Liebig (*P.* 21, 1), hydrogen being weighed as H_2O and carbon as CO_2. The operation is performed in a closed or in an open tube.

Closed tube, combustion.

A tube of hard glass (diameter ·5 inch) is drawn out as represented, the length being about 18 inches. It is thoroughly cleaned by washing with fuming HNO_3, water, alcohol, and ether; and is then dried. Coarsely powdered oxide of copper, which has been prepared by oxidising the metal, not by strongly heating the nitrate, and has been dried at a red heat, is poured in as far as *a*; a mixture of the weighed substance with finely powdered dry CuO is then poured in, it fills up the space from *a* to *b*; the vessel (mortar or glass tube) in which the mixture has been effected is then rinsed with more finely divided CuO, and these rinsings are poured into the tube and take up the space *b* to *c*; finally some coarse CuO is poured in, taking the space *c* to *d*. The tube is then gently tapped to ensure free passage for gas from end to end. A tube containing $CaCl_2$ is fixed by means of a cork to the open end of the combustion tube, and a bulb-apparatus (Liebig's or Geissler's) containing caustic potash (1 pt. KOH to 2 pts. H_2O) is attached to this, and in accurate experiments a drying tube containing $CaCl_2$ or solid KOH is placed beyond the potash-bulbs.

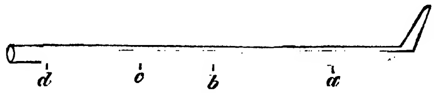
The oxide of copper at *d* is first heated to redness, and then the tube is heated at the other end; the gas-burners of the furnace are then

gradually turned on, at either end, so that a regular stream of bubbles passes into the potash bulbs. When the entire tube has reached a dull red heat, the potash solution will begin to be sucked back, owing to absorption of CO_2; at this moment the point of the tube is broken off, and air is sucked through the entire apparatus in order that the gases still contained in the tube may be drawn into the weighed bulbs; in this operation a long glass tube, open at both ends, may be placed over the broken point of the tube to prevent furnace gases being sucked in. The calcium chloride tube and potash bulbs are weighed when cool: $\frac{1}{9}$ of the increase of weight of the former is hydrogen, $\frac{3}{11}$ of the increase of weight of the latter is carbon.

Open tube, combustion.

It is in every way better to make the combustion in an 'open tube,' that is a tube through which oxygen is continually passing.

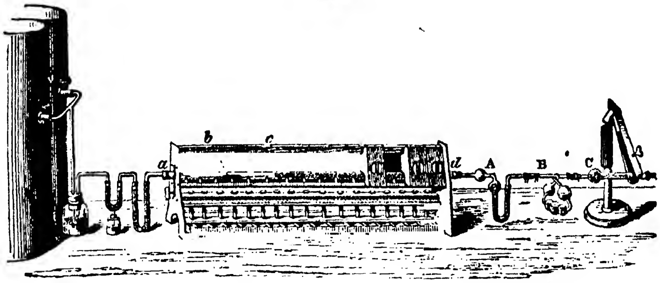
The greater part of such a tube is filled with oxide of copper, $c\ d$; this is followed by an open space of about 2 inches; then comes a porcelain or platinum boat, b, containing the weighed substance; beyond (between b and a) it is advisable to have a spiral of oxidised copper. The boat and its contents are not inserted until the whole tube has been red hot for some time, during which a current of dry oxygen, free from carbonic acid, has been passing through it; it is of course necessary to allow the end $a\ c$ of the tube to cool down before inserting the substance, otherwise this would be volatilised too rapidly. While the tube is cooling, the calcium chloride tube A, potash bulbs B, and the drying tube C are attached. The tube, which is still red-hot from c to d, is now heated at a and the burners are lighted one after another until the whole tube is red hot. A slow current of oxygen is passed in at a during the combustion. The combustion is continued until oxygen escaping from C will rekindle a glowing match. Before weighing, the oxygen in the tubes A, C, but especially B, must be displaced by air; in a properly conducted experiment C will not gain more than ·01 g., a greater increase indicates spurting of the potash due to a too rapid current of gas. At the end of one experiment the tube is quite ready for a second.



Liquids of high boiling-point are analysed in the same way as solids, except that they are weighed in short open tubes; volatile liquids such as ether are best put into a bulb or V-tube, which is inserted between the oxygen apparatus and the combustion tube; the proportion between oxygen and vapour of the substance depends upon the temperature of the bulb-tube and should be so regulated that the oxygen should be always in considerable excess, otherwise an explosion might occur.

The potash-bulbs may be replaced by a U-tube containing soda-lime; in this case the escaping gas must be allowed to bubble through H_2SO_4 in order that the rate at which it is coming off may be noted.

Minute quantities of carbonic acid are absorbed by CuO and even by $PbCrO_4$ and retained at a red heat. Hence in the determination of minute quantities of carbon (as in the residue from drinking water) these substances should be previously ignited in a current of air (Dittmar a. Robinson, *C. N.* 36, 26).



Minute quantities of carbon may also be estimated by burning in an open combustion tube in a current of oxygen, in the usual way, and absorbing the CO_2 in baryta water. The $BaCO_3$ is filtered off, converted into sulphate and weighed (Dupré a. Hake, *C. J.* 35, 159). Other methods are described below.

Combustion with Chromic Acid.

Carbon may be determined by heating the substance with CrO_3 and H_2SO_4 and measuring the mixture of CO and CO_2 given off (Cross a. Bevan, *C. N.* 52, 207).

Substances containing Nitrogen.

Determination of Carbon and Hydrogen.

If the substance contains nitrogen, **nitrous** fumes might be evolved, and those would be absorbed in the weighed tubes. To prevent this, **a layer of metallic copper is put in the front of the tube, near d, and kept red-hot: it reduces oxides of nitrogen to nitrogen. This copper is best**

obtained by heating a roll of wire gauze in a Bunsen flame, and reducing the oxidised surface in a current of hydrogen; it should then be allowed to cool in a current of CO_2, as it would absorb hydrogen if left to cool in that gas. The copper spiral may also be reduced by heating it in the mixture of CO and CO_2 obtained by warming oxalic acid with H_2SO_4 (C. E. Groves, *C. J.* 37, 505).

Binoxide of manganese mixed with potassic chromate may be used instead of a reduced copper spiral in combustion of nitrogenous substances. The mixture is made by stirring precipitated binoxide of manganese with a saturated solution of potassic chromate containing a little bichromate; the paste is dried and heated somewhat strongly. The combustion is performed with plumbic chromate (or copper oxide) in the usual way, about 5 inches of the chromate mixture being put in the front part of the tube to absorb the nitrous fumes. In performing a combustion, the whole tube is strongly heated, while pure air is passed through it, then the absorbent mixture is allowed to cool to 200°-250° and kept at that temperature during the combustion (Perkin, *C. J.* 37, 457).

Estimation of Nitrogen.

Will and Varrentrapp (*A.* 39, 257) mix the substance with soda lime, that has recently been strongly heated, and put the mixture into a short combustion-tube drawn out to a point at one end. The operation is conducted exactly as in combustion in a closed tube (*v. supra*), the escaping gases being passed into a bulb-apparatus to absorb ammonia. The bulbs contain hydrochloric acid, the NH_3 being weighed as $(NH_4)_2PtCl_6$; or, better, standard hydrochloric or oxalic acid, the amount of NH_3 being then determined by subsequent titration.

If the soda-lime contain nitrate it will evolve NH_3 even when heated with sugar (Schulze a. Kreussler, *Fr.* 12, 362). If in preparing the soda-lime a little $Na_2S_2O_3$ be added before evaporating and strongly heating, small quantities of nitrates and nitrites will be reduced and eliminated as NH_3 (Dittmar, *priv. com.*). Substances rich in nitrogen should be mixed with sugar after weighing.

Unfortunately many organic compounds do not yield all their nitrogen in the form of ammonia when ignited with soda-lime; such are nitroso-, nitro-, azo- and diazo-, compounds, and even some proteids (Ritthausen, *Fr.* 17, 501; Kreussler, *J.* 1884, 1608); in this case the method of analysis proposed by Dumas is generally used. Modifications of the soda-lime process intended to overcome this difficulty have, however, been proposed. Ruffle (*C. J.* 39, 87) mixes the substance (1 g.) with sulphur (·75 g.) and finely powdered wood charcoal (·75 g.). Soda-lime prepared from NaOH (160 g.), water and CaO (56 g.) is dried and mixed with $Na_2S_2O_3$(21 g.). Two-thirds of the tube is filled with this mixture, containing the substance to be analysed; the remaining third is ordinary soda-lime, which prevents evolution of H_2S. The thiosulphate reduces nitro compounds.

Arnold (*B.* 18, 806) prefers a mixture of soda-lime, sodium formate and $Na_2S_2O_3$.

Dumas (*A. Ch.* [2] 53, 171) heats the substance with oxide of copper and measures the escaping nitrogen. A combustion-tube closed at one end has first some bicarbonate of soda, or, much better, magnesite, put into it; this is followed by pure oxide of copper, a mixture of oxide of copper and the weighed substance, pure oxide of copper, and finally a bright copper spiral —just as in an ordinary combustion; the end of the tube is closed by a cork through which passes a delivery tube dipping under mercury. Before beginning the combustion all the air must be driven out of the tube by carbonic acid; this is effected by heating the magnesite; the combustion is then proceeded with in the ordinary way, and the gaseous products are collected in a graduated tube standing over mercury and containing 50 c.c. of a solution of caustic potash (equal weights of potash and water). The products of combustion are water, carbonic acid, and nitrogen; the two former are stopped by the potash, so that the gas that collects is pure nitrogen; at the end of the experiment the combustion tube still contains nitrogen which must be expelled by heating the magnesite a second time. The eudiometer and its contents is then transferred to a vessel containing air-free water, which takes the place of the mercury and potash. The volume of the nitrogen corrected for pressure and temperature enables one to calculate its weight.

As there is some danger that the magnesite may be all used up in the preliminary expulsion of air from the tube, a convenient modification of this process consists in expelling the air by hydrogen; the hydrogen is got rid of by igniting a little of the copper oxide in the front part of the tube; a complete vacuum is thus formed, and the mercury rises in the delivery tube to the height of the barometer. The combustion is proceeded with in the usual way, and the residual nitrogen expelled by heating the magnesite.

Bicarbonate of soda, $MnCO_3$, or a mixture of Na_2CO_3 and $K_2Cr_2O_7$ may be used instead of magnesite as a source of CO_2. In order that the tube may be used several times without turning out all the copper oxide, C. E. Groves (*C. J.* 37, 504) places the substance intended to evolve CO_2 in a separate tube, 7 inches long, which is attached by a short glass connecting-tube to the end of the combustion-tube, which is in this case open at both ends. A fresh carbonic acid tube is used for each experiment. The CO_2 may also be obtained from marble and HCl aq or H_2SO_4, but it is then liable to contain air unless the apparatus be first exhausted by an air-pump (Bernthsen, *Fr.* 21, 63) or heated to boiling (Hufschmidt, *B.* 18, 1441). The nitrogen is frequently contaminated with NO. Frankland a. Armstrong (*C. J.* 21, 77), after reading off the nitrogen, pass up a little oxygen, and, when the resulting NO_2 has been absorbed, they remove the excess of oxygen by potassium pyrogallate. The mean between the volumes of gas before and after this operation is the true volume of nitrogen (Thudichum a. Wanklyn, *C. J.* 22, 293). Apparatus for collecting and measuring the nitrogen have been devised by Zulkowsky (*A.* 182, 296), Schwarz (*B.* 13, 771), Ludwig, (*B.* 13, 883), H. Schiff (*B.* 13, 885), C. E. Groves (*C. J.* 37, 500), Staedel (*Fr.* 19, 452),

Schmitt (*J. pr.* [2] 24, 444), Gladding (*Am.* 4, 42), Hempel (*Fr.* 17, 409), and Ilinski (*B.* 17, 1847). Frankland a. Armstrong (*C. J.* 21, 77) connect the tube with a Sprengel's pump, which delivers the gas into a eudiometer at the end of the dropping tube (see also Gibbs, *Fr.* 11, 206; Hempel, *Bn.* 1, 9; Pflüger, *Fr.* 18, 296; Johnson a. Jenkins, *Am.* 2, 27). Explosive substances may be analysed under diminished pressure.

The weight of nitrogen is calculated from its volume with the aid of the annexed table. From the barometric height, corrected for expansion of mercury and of the scale, the vapour pressure of water at the temperature of the nitrogen is deducted; from the corrected pressure and the temperature the weight of nitrogen is at once given by the table.

Pressure of Aqueous Vapour, in mm.

Temp.	10°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°
Pressure	9·2	9·8	10·5	11·2	11·9	12·7	13·5	14·4	15·4	16·3	17·4	18·5	19·7	20·9	22·2	23·6

Reduction of Barometric Height.

If the barometer has a glass scale, the necessary reduction will be found by multiplying the following numbers by the temperature, viz.:—

mm.	Reduction	mm.	Reduction
720	·123	750	·128
725	·124	755	·129
730	·125	760	·130
735	·126	765	·131
740	·127	770	·132
745	·127	775	·133

Vapour-Pressure of Aqueous KOH.

When nitrogen is measured over aqueous potash, the correction for vapour-pressure is less than that given above, as is seen from the following table, which relates to a solution of 1 pt. of potash in 2½ pts. water (S.G. 1·258).

10°	6·19	18°	10·47
11°	6·58	19°	11·20
12°	7·02	20°	11·97
13°	7·48	21°	12·80
14°	7·99	22°	13·70
15°	8·53	23°	14·62
16°	9·13	24°	15·60
17°	9·77	25°	16·65

(Kreusler, *Fr.* 24, 445).

In the course of an elaborate discussion of the various methods of estimating nitrogen, Kreusler (*Landwirthschaftliche Versuchstationen*, 31, 207; *cf. Fr.* 19, 92; 24, 438) recommends that the copper oxide be mixed with asbestos. Cupric sulphate (150 g.), water (400 g.), and light asbestos (50 g.), are evaporated until almost dry; the mass is then thrown in small quantities into boiling water (2500 g.) containing KOH (160 g.), and finally washed, dried, and heated until red hot. Kreusler also uses copper-asbestos prepared by reducing this copper-oxide-asbestos in place of a copper spiral.

Nitrogen may often be converted into NH_3 by $KMnO_4$ and boiling NaOHAq (Wanklyn, Chapman, a. Smith, *C. J.* 20, 445), or by $KMnO_4$ and fuming H_2SO_4 (Kjeldahl, *Fr.* 22, 370). In the latter case it is better to add $CuSO_4$ (Hilfahrt, C. C 16, 17), benzoic acid, sugar, and mercury (Arnold, *Ar. Ph.* [2] 24, 785). Kreusler recommends a mixture of conc. H_2SO_4 (9 pts.) and P_2O_5 (1 pt.) as a substitute for fuming H_2SO_4 (*v.* also Warington, *C. N.* 52, 162).

Substances containing Halogens.

Determination of Carbon and Hydrogen.

In the combustion of substances containing chlorine white fumes of cuprous chloride might pass into the chloride of calcium tube, and even chlorine might be given off by the action of the oxygen (Städeler, *A.* 69, 335; Kraut, *Fr.* 2, 242); these sources of error may be prevented by placing a roll of silver foil between the copper oxide and the cork into which the chloride of calcium tube is inserted. This part of the tube is kept at a dull red heat throughout the combustion; cuprous chloride and silver form silver chloride and copper.

If the substance contains nitrogen as well as halogens, a copper spiral need not precede the silver spiral.

Determination of Halogens.

This is usually effected by placing 4 c.c. fuming nitric acid and about a gram of silver nitrate in a strong glass tube, then sliding down a little tube containing the weighed substance in such a manner that it may stick to the wet glass and not at once fall into the acid; the open end of the strong glass tube is then fused, drawn off to a stout point and sealed. A little tapping will now cause the tube containing the substance to fall into the acid, after which the whole is heated at 180° for seven hours in a gun-barrel. Aromatic substances require a higher temperature, 250°–300°. Silver chloride (bromide or iodide) is formed, and, after opening the tube, diluting and boiling, it is collected, dried, and weighed (Carius, *A.* 116, 1; 136, 129). A still easier method is that lately proposed by Plimpton and Graves (*C. J.* 43, 119), in which the organic substance is burnt in the flame of a small Bunsen burner; the halogen is left chiefly combined with hydrogen but partly in the free state. The products are sucked through aqueous NaOH, which is then boiled with SO_2 and subsequently mixed with HNO_3. The halogen is then estimated volumetrically (best by sulphocyanide method) or gravimetrically.

Another method is to heat the substance in a combustion tube through which oxygen charged with nitrous fumes is passing (Klason, *B.* 19, 1910).

Halogens may in many cases be determined by strongly heating with lime; with a mixture of Na_2CO_3 and KNO_3 (Volhard, *A.* 190, 40); with Fe_2O_3 (E. Kopp, *B.* 8, 769; Klobulowski, *B.* 10, 290); or with alcoholic KOH; or by reducing with sodium amalgam (Kekulé, *A. Suppl.* 1, 340).

Halogens in the side-chains of aromatic compounds may be estimated by boiling with a saturated alcoholic solution of $AgNO_3$ (Schulze, *B.* 17, 1675).

Table showing the weight in milligrammes of 1 c.c. nitrogen at 10° to 25° C. and 720 to 770 mm. pressure (Dietrich, *Fr.* 5, 38).

	10°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	
770	1·21355	1·20829	1·20294	1·19768	1·19234	1·18694	1·18156	1·17608	1·17056	1·16504	1·15948	1·15385	1·14818	1·14241	1·13659	1·13073	770
768	1·21036	1·20511	1·19977	1·19452	1·18920	1·18381	1·17844	1·17297	1·16746	1·16195	1·15640	1·15078	1·14512	1·13936	1·13355	1·12770	768
766	1·20717	1·20193	1·19660	1·19136	1·18605	1·18067	1·17531	1·16985	1·16436	1·15886	1·15332	1·14771	1·14206	1·13631	1·13051	1·12467	766
764	1·20398	1·19875	1·19344	1·18820	1·18291	1·17754	1·17219	1·16674	1·16126	1·15576	1·15024	1·14464	1·13900	1·13326	1·12747	1·12164	764
762	1·20079	1·19557	1·19027	1·18505	1·17976	1·17440	1·16906	1·16363	1·15816	1·15267	1·14716	1·14157	1·13594	1·13021	1·12443	1·11861	762
760	1·19760	1·19239	1·18710	1·18189	1·17661	1·17127	1·16594	1·16052	1·15506	1·14958	1·14408	1·13850	1·13288	1·12716	1·12139	1·11558	760
758	1·19441	1·18921	1·18394	1·17873	1·17347	1·16814	1·16282	1·15741	1·15196	1·14649	1·14099	1·13543	1·12982	1·12411	1·11835	1·11255	758
756	1·19122	1·18603	1·18077	1·17558	1·17032	1·16500	1·15969	1·15429	1·14886	1·14340	1·13791	1·13236	1·12675	1·12106	1·11532	1·10952	756
754	1·18803	1·18286	1·17760	1·17242	1·16718	1·16187	1·15657	1·15118	1·14576	1·14030	1·13483	1·12928	1·12369	1·11801	1·11228	1·10649	754
752	1·18484	1·17968	1·17444	1·16926	1·16403	1·15873	1·15344	1·14807	1·14266	1·13721	1·13175	1·12621	1·12063	1·11496	1·10924	1·10346	752
750	1·18165	1·17650	1·17127	1·16611	1·16088	1·15560	1·15032	1·14496	1·13955	1·13412	1·12867	1·12314	1·11757	1·11191	1·10620	1·10043	750
748	1·17846	1·17332	1·16810	1·16295	1·15774	1·15247	1·14720	1·14185	1·13645	1·13103	1·12559	1·12007	1·11451	1·10886	1·10316	1·09740	748
746	1·17527	1·17014	1·16493	1·15979	1·15459	1·14933	1·14407	1·13873	1·13335	1·12794	1·12251	1·11700	1·11145	1·10581	1·10012	1·09437	746
744	1·17208	1·16696	1·16177	1·15663	1·15145	1·14620	1·14095	1·13562	1·13025	1·12484	1·11943	1·11393	1·10839	1·10276	1·09708	1·09134	744
742	1·16889	1·16378	1·15860	1·15348	1·14830	1·14306	1·13782	1·13251	1·12715	1·12175	1·11635	1·11086	1·10533	1·09971	1·09404	1·08831	742
740	1·16570	1·16060	1·15543	1·15032	1·14515	1·13993	1·13470	1·12940	1·12405	1·11866	1·11327	1·10779	1·10227	1·09666	1·09100	1·08528	740
738	1·16251	1·15742	1·15227	1·14716	1·14201	1·13680	1·13158	1·12629	1·12095	1·11557	1·11018	1·10472	1·09921	1·09361	1·08796	1·08225	738
736	1·15932	1·15424	1·14910	1·14401	1·13886	1·13366	1·12845	1·12317	1·11785	1·11248	1·10710	1·10165	1·09614	1·09056	1·08493	1·07922	736
734	1·15613	1·15107	1·14593	1·14085	1·13572	1·13053	1·12533	1·12006	1·11475	1·10938	1·10402	1·09857	1·09308	1·08751	1·08189	1·07619	734
732	1·15294	1·14789	1·14277	1·13769	1·13257	1·12739	1·12220	1·11695	1·11165	1·10629	1·10094	1·09550	1·09002	1·08446	1·07885	1·07316	732
730	1·14975	1·14471	1·13960	1·13454	1·12942	1·12426	1·11908	1·11384	1·10854	1·10320	1·09786	1·09243	1·08696	1·08141	1·07581	1·07013	730
728	1·14656	1·14153	1·13643	1·13138	1·12628	1·12113	1·11596	1·11073	1·10544	1·10011	1·09478	1·08936	1·08390	1·07836	1·07277	1·06710	728
726	1·14337	1·13835	1·13326	1·12822	1·12313	1·11799	1·11283	1·10761	1·10234	1·09702	1·09170	1·08629	1·08084	1·07531	1·06973	1·06407	726
724	1·14018	1·13517	1·13010	1·12506	1·11999	1·11486	1·10971	1·10450	1·09924	1·09392	1·08862	1·08322	1·07778	1·07226	1·06669	1·06104	724
722	1·13699	1·13199	1·12693	1·12191	1·11684	1·11172	1·10658	1·10139	1·09614	1·09083	1·08554	1·08015	1·07472	1·06921	1·06365	1·05801	722
720	1·13380	1·12881	1·12376	1·11875	1·11369	1·10859	1·10346	1·09828	1·09304	1·08774	1·08246	1·07708	1·07166	1·06616	1·06061	1·05499	720

Compounds containing Sulphur.

Determination of Carbon and Hydrogen.

In the analysis of compounds containing sulphur there is danger that SO_2 may be absorbed in the weighed tubes. This is obviated by using lead chromate, in the form of small fused lumps, instead of cupric oxide. The $PbCrO_4$ (10 pts.) may be mixed with $K_2Cr_2O_7$ (1 pt.). Sulphur remains in the tube as $PbSO_4$. Volatile substances containing N as well as S must be burnt slowly (V. Meyer a. Städeler, *B.* 17, 1577). According to Ritthausen (*Fr.* 22, 108), reduced lead chromate can be re-oxidised by heating in a current of oxygen. It is of course not necessary to fill the whole tube with lead chromate, the posterior half may contain CuO. A mixture of CuO and $PbCrO_4$ is sometimes used.

Determination of Sulphur.

Sulphur may be estimated by the method of Carius, by heating with fuming HNO_3 in a tube as described for halogens; the sulphuric acid is ppd. by $BaCl_2$. This method cannot usually be employed in the case of organic sulphides, since these are converted into sulphonic acids.

The most rapid method is that of Plimpton, which consists in burning the substance in the flame of a small Bunsen, sucking the products of combustion through dilute NaOHAq, oxidising with Cl, and ppg. as $BaSO_4$ (Morley a. Saint, *C. J.* 43, 401). Or the substance may be burnt in a stream of oxygen and the SO_2 collected in HClAq containing Br (Sauer, *Fr.* 12, 32, 178; Mixter, *Fr.* 22, 581). In this experiment it is better to pass the oxygen through fuming nitric acid so that it may be charged with nitrous fumes (Klason, *B.* 19, 1910). In many cases sulphur may be determined by fusion with a mixture of Na_2CO_3 and KNO_3 or $KClO_3$. In the case of albuminoids it is convenient to evaporate with HNO_3 (10 pts. of S. G. 1·4) before fusing (Kochs, *C. C.* 1886, 894). Oxidation may also be effected by Na_2CO_3 and HgO (Russell, *C. J.* 7, 212).

Phosphorus.

The estimation of phosphorus resembles that of S. It is weighed as $Mg_2P_2O_7$.

Boron.

If compounds containing boron are analysed by combustion with copper oxide the hydrogen will come out too high, owing to the volatilisation of boric acid. This is prevented by using lead chromate instead of cupric oxide (Councler, *J. pr.* [2] 18, 375).

Silicon.

SiO_2 is left behind when non-volatile compounds are heated. Volatile compounds are heated with conc. or fuming H_2SO_4 and KMnO ; the product is poured into water. The ppd. H_2SiO_3 is freed from traces of manganese by fusion with Na_2CO_3 and KNO_3 (Polis, *B.* 19, 1024).

Alkalis or Alkaline Earths.

In an ordinary combustion these would be left as carbonates, the estimation of carbon thus being too low; but if the substance is thoroughly mixed with $PbCrO_4$ (10 pts.), and $K_2Cr_2O_7$ (1 pt.), the CO_2 will be turned out by CrO_3, the bases being left as chromates. Schaller (*Bl.* [2] 2, 93) mixes the alkaline salts of organic acids with an equal weight of SiO_2 and then with CuO.

The alkaline metals are determined by strongly heating and analysing the inorganic residue.

Silver, Platinum, and Gold

Are determined by strongly heating the substance and weighing the metallic residue.

Explosive Substances

Must be well mixed with CuO before being put into a combustion tube; very explosive substances are analysed *in vacuo.*

Combustion with platinum black.

Kopfer (*C. J.* 29, 660) introduced the use of finely divided platinum as a carrier of oxygen. The anterior half of a combustion-tube is filled with platinum black intimately mixed with asbestos, the posterior half of the tube contains the weighed substance in a boat; air or oxygen is passed through the tube, the combustion being conducted in the usual way.

Additional References.

Gay-Lussac a. Thenard, *A. Ch.* 74, 47 ($KClO_3$); Saussure, *A. Ch.* 78, 57; Berzelius, Thomson's *Annals of Philosophy*, 4, 401, *P.* 44, 391; Liebig, *P.* 21, 1; Liebig a. Wöhler, *A.* 26, 270; Hofmann, *C. J.* 11, 30; Cloez, *A. Ch.* [3] 68, 394 (iron tube); *Bl.* [2] 1, 250; Fr. Schulze, *Fr.* 5, 289 ($KClO_3$); Wheeler, *Am. S.* [2] 41, 33; Marchand, *J. pr.* 41, 177; Gottlieb, *A.* 78, 241; Melsens, *A.* 60, 115; Frankland, *T.* 147, 63; Thorp, *C. J.* 19, 359; Maxwell Simpson, *C. J.* 6, 289; *A.* 95, 63; Pflüger, *Arch. ges. Phys.* 1878, 117; H. Schiff, *A.* 195, 293; Warren, *Am. S.* [2] 42, 156.

Determination of oxygen: Wanklyn a. Frank, *P. M.* [4] 26, 554; Baumhauer, *A.* 90, 228; *Ar. N.* 1, 179; Ladenburg, *A.* 135, 1 ($AgIO_3$); A. Mitscherlich, *P.* 130, 536; *B.* 1, 45; 6, 1000; Cretier, *Fr.* 13, 1; Stromeyer, *A.* 117, 247.

Simultaneous determination of C, H, and N: (Schulze, *Fr.* 5, 269; Frerichs, *B.* 10, 26; Hempel, *Fr.* 17, 409; Jannasch a. V. Meyer, *B.* 19, 949).

Proximate Analysis.

Separation of Mixtures.

A complete account of proximate organic analysis would include descriptions of the properties of every known organic substance, since the methods to be adopted vary in almost every case.

The simplest method is separation by solvents which dissolve some but not all of the components of a mixture; when solid substances have been dissolved, they may usually be further purified by crystallisation.

An unknown mixture is treated with water; the insoluble portion is shaken with dilute H_2SO_4 which dissolves bases, then with dilute Na_2CO_3 which dissolves acids, then with dilute NaOH which dissolves phenols; the bases are ppd. by adding KOH to the H_2SO_4Aq; the acids and phenols by acidifying the alkaline solutions containing them.

The neutral residue is fractionally distilled and the various portions are boiled with alcoholic KOH which saponifies compound ethers, and gives a pp. of KCl in the case of fatty chloro-derivatives. The alcohol is distilled off together with volatile alcohols, &c., and the residue treated with water, which dissolves salts of acids that may have been formed. The insoluble residue is a hydrocarbon, high-boiling alcohol, alkyl oxide, ketone, haloid aromatic compound, &c.; the hydrocarbon will usually be left on treating the residue with cold H_2SO_4 if aromatic chloro-derivatives are absent.

The aqueous extract of the original substance is neutralised (if necessary) and distilled. The distillate is treated with K_2CO_3 which separates alcohols, lactones, methyl acetate &c. The residue is made alkaline by KOH and distilled: bases pass over; it is then acidified with H_2SO_4 and distilled: volatile acids pass over. The residue is exactly neutralised and neutral substances are extracted by ether, chloroform, and benzene, the aqueous residue is acidified and non-volatile acids are extracted by these solvents; the residue is now made alkaline and again extracted, finally it is evaporated to dryness, and, if any organic matter is still present, extracted with solvents. (*V.* also ALKALOIDS, p. 120; ACIDS, p. 56.)

Many substances, even of very high boiling point, distil in a current of steam.

Detection of radicles.

Hydroxyl.—Compounds containing OH evolve HCl when treated with PCl_3 (p. 54); but if PCl_5 is used chlorination may occur *e.g.* $C_6H_5OMe + PCl_5 = C_6H_4Cl.OMe + PCl_3 + HCl$. AcCl acts upon hydroxylic compounds with evolution of HCl; when water is added to the product the acetyl derivatives of alcoholic hydroxyls are not affected, but CO.OAc is converted into CO.OH. AcCl acts also upon amines in the following way:

$$C_6H_5NH_2 + AcCl = C_6H_5NAcH + HCl.$$

BzCl and Ac_2O also displace hydroxylic hydrogen by acid radicles. In compounds whose molecules do not contain NH_2 or NH the number of hydroxyls (other than those in carboxyls) present can be determined by estimating the acetic acid obtained by saponifying the product after treatment with water. The groups C.CO.NH and $C.CO.CH_2$ in many cases act as if they contained hydroxyl and were C.C(OH):N and C.C(OH):CH.

Very dilute, colourless solutions of Fe_2Cl_6 give a distinct colouration with compounds containing alcoholic hydroxyl (Landwehr, *B.* 19, 2726).

Zinc ethide evolves ethane gas when mixed with compounds containing hydroxyl or amidogen (Japp, *C. J.* 37, 665); compounds containing imidogen evolve gas when heated with $ZnEt_2$ at 100° (Japp, *C. J.* 39, 224). (*V.* also ALCOHOLS and ACIDS.)

Amidogen is indicated by the reactions just mentioned, and also by the readiness with which methyl can be introduced by heating with MeI. Methyl iodide does not act upon hydroxyl except in presence of an alkali. Compounds containing NH_2 evolve nitrogen when heated with nitrous acid.

The number of amidogens in the molecule of a compound may be found by treating the substance with KNO_2 and H_2SO_4; the escaping nitrogen is freed from NO by $FeSO_4$ and then measured (Sachsse a. Kormann, *Fr.* 14, 380). In easily diazotised aromatic amido compounds, the number of amidogens may be determined by dissolving in conc. HClAq and titrating with a normal solution of KNO_2, until a drop of the solution gives a blue colour with KI and starch (Green a. Evershed, *S. C. I.* 5, 633).

Imidogen is indicated by the production of a nitrosamine when treated with nitrous acid. (See also AMINES, AMIDO-ACIDS, AMIDES.)

Carbonyl is indicated by the reaction with phenyl-hydrazine and hydroxylamine (p. 107).

Carboxyl is indicated by the easy production of metallic salts, and by the splitting off of CO_2 when the substance is heated alone or with lime.

Want of saturation is indicated by instant bleaching of bromine.

Acetylenic hydrogen is indicated by the formation of explosive pps. with ammoniacal cuprous chloride or silver nitrate.

Nitroxyl.—Nitro compounds may be reduced to compounds containing amidogen. The number of nitroxyls is found by reducing with standard $SnCl_2$ and titrating with iodine (Limpricht, *B.* 11, 35).

Methoxyl. The number of MeO groups can be found by boiling with aqueous HI (S.G. 1·68) the distillate (MeI) being received in alcoholic $AgNO_3$ and the resulting AgI weighed (Zeisel, *M.* 6, 989).

Halogens in the side chains of aromatic compounds can be estimated by boiling with a saturated alcoholic solution of $AgNO_3$ (Schulze, *B.* 17, 1675).

ANAMIRTIN $C_{19}H_{24}O_{10}$(?). Occurs in grains of cocculus indicus (*Anamirta cocculus*) along with picrotoxin (*q. v.*), picrotin, and glyceryl stearate (Barth a. Kretschy, *Sitz. B.* [ii] 81, 7; Francis, *A.* 42, 254). Short needles (from water), insol. benzene; becomes brown at 260°. Neither bitter nor poisonous.

ANCHOÏC ACID = AZELAÏC ACID.

ANCHUSIN *v.* ALKANET.

ANDROMEDOTOXIN $C_{31}H_{51}O_{10}$ [228°]. A poisonous substance in *Rhododendron ponticum* (Zaaijer, *R.* 5, 313).

ANEMONE.—The plants *Anemone nemorosa*, *A. pratensis*, and *A. pulsatilla* when distilled with steam yield anemonin, anemone-camphor, anemonic acid, and a yellowish oil, which are extracted by shaking the distillate with chloroform (Löwig a. Weidmann, *P.* 46, 45; Schwarz, *Mag. Pharm.* 10, 193; 19, 168; Fehling, *A.* 38, 278; Dobraschinsky, *J. Ph.* [4] 1, 319; H. Beckurts, *C. C.* 1885, 776).

Anemonin $C_{15}H_{12}O_6$. [150°]. Trimetric crystals; sol. $CHCl_3$, sl. sol. alcohol and water, insol. ether. Reduces $AgNO_3$.—$PbOC_{15}H_{12}O_6$.

Anemonic acid. Amorphous powder; insol. water, alcohol, and ether.

Anemone-camphor. Trimetric prisms; unstable.

ANETHOL $C_{10}H_{12}O$ *i.e.* $CH_3O.C_6H_4.CH:CH.CH_3$ [1:4]. *Methyl p-propenyl-phenol.* [21·3°]. (232°). S.G. ^{21} ·987. μ_H 1·6167 (Gladstone, *C. J.* 49, 623). R_∞ 77·97 (Nasini, *G.* 15, 93). S.V.S. 149·34.

Occurrence.—In oil of anise (from *Pimpinella anisum*) together with a terpene, in China or star anise (from *Illicium anisatum*), in fennel (*Anethum fœniculum*), and tarragon (*Artemisia Dracunculus*) (Laurent, *Revue Scient.* 10, 6; Gerhardt, *A.* 44, 318; 52, 401; Cahours, *A. Ch.* [3] 2, 274).

Formation. — Together with CO_2 when $CH_3O.C_6H_4.CH:C(CH_3).CO_2H$ is heated (Perkin, *C. J.* 32, 669).

Properties.—Plates; v. sl. sol. water, v. e. sol. alcohol and ether. Easily polymerised.

Reactions. — 1. *Oxidation* produces anisic aldehyde, anisic acid, and acetic acid (Hempel, *A.* 59, 104). — 2. *Alcoholic potash* produces $C_{16}H_{18}O_3$ [87°] and $C_{14}H_{16}O_2$ [65°]; the latter forms an acetyl derivative [40°] (Landolph, *B.* 13, 147; *C. R.* 81, 97; 82, 226).—3. *Nitrosyl chloride* produces $C_6H_4(OMe).C_3H_5NOCl$ which reduces to $C_6H_4(OMe).C_3H_6NH_2$ (Tönnies, *B.* 12, 169).—4. *Nitrous acid* produces two bodies: $C_6H_4(OMe).C_3H_5N_2O_3$ and $C_6H_4(OMe).C_3H_3N_2O_2$ [97°]. The former may be reduced to $C_6H_4(OMe).C_3H_5(OH)NH_2HCl$, the latter to $(CH_3O.C_6H_4.C_3H_3)_2N_4O_3$ (?) (T., *B.* 13, 1845).—5. *Boron fluoride* produces C_6H_5OMe, and a liquid $C_{11}H_{16}O$ (c. 227°) (L., *C. R.* 86, 601).—6. HI at 260° forms C_8H_{16} (150°) and $C_{12}H_{22}$ (210°) (L., *C. R.* 82, 849). — 7. PCl_5 forms $C_{10}H_{11}ClO$, [-3°], (229°), S.G. $\frac{20}{}$ 1·191 (Landolph); Ladenburg gives different properties for chloro-anethol, viz.: [6°], (258°), S.G. $\frac{0}{}$ 1·125.—8. Br forms $C_{10}H_{12}Br_2O$, [65°] (Ladenburg, *A. Suppl.* 8, 87; *Z.* [2] 5, 576).

Anethol - tetrahydride $C_{10}H_{16}O$. *Anethol-camphor.* [190°-193°]. Has a camphor-like smell. Formed together with anisic aldehyde by the oxidation of anethol with HNO_3 (L.). Smells like camphor. On oxidation with $K_2Cr_2O_7$ it gives an acid which forms long needles of melting point [175°] (anisic acid ?).

Anethol - hexahydride $C_{10}H_{18}O$. *Anethol-borneol* [19°]. (198°). Formed together with an acid by heating anethol - tetrahydride with alcoholic KOH (L.). Long slender needles. Insol. KOHAq.

Anethol dihydride = *Methyl*-PROPYL-PHENOL.

Anethoïn $(C_{10}H_{12}O)_n$. *Anisoïn.* [140°-145°]. From anethol by shaking with a little H_2SO_4 or P_2O_5 (C.), or by the action of $SnCl_4$ (Gerhardt, *J. pr.* 36, 267), I in KIAq (Will a. Rhodius, *A.* 65, 230) or BzCl (Kraut a. Uelsmann, *J. pr.* 77, 490). Prepared by distilling oil of anise with conc. H_2SO_4. Needles (from ether); insol. water and alcohol. Decomposed on distillation into liquid metanethol and solid isanethol.

Metanethol $(C_{10}H_{12}O)_n$. [132°]. (above 300°). Prepared by heating anethol (210 g.) with $ZnCl_2$ (750 g.) in a copper retort; in a few minutes white fumes appear in the receiver, superheated steam is then passed into the retort; the metanethol then passes slowly over. The yield is 5 to 10 p.c. (Perrenoud, *A.* 187, 63). Silky needles (from ether). Not volatile with steam at 100°.

Metanethol sulphonic acid $(C_{10}H_{11}(SO_3H)O)_n$. Formed by conc. H_2SO_4 in the cold. Salts.—CaA'_2aq: laminæ.—BaA'_2.

Chloride $C_{10}H_{11}(SO_2Cl)O$. [183°].

Liquid metanethol $(C_{10}H_{12}O)_n$. (233°). S.G. $\frac{18}{}$ ·971. Formed by distilling anethoïn (Kraut a. Schlun, *Z.* 1863, 359); and by distilling anethol with $ZnCl_2$. Converted by conc. H_2SO_4 into anethoïn. At 320° it partially changes to isanethol.

Sulphonic acid.—$(C_{10}H_{11}(SO_3H)O)_n$ (Gerhardt, *J. pr.* 36, 275). Salt.—CaA'_2aq: gummy.

Isanethol $(C_{10}H_{12}O)_n$. A viscid mass left in the retort when anethoïn is distilled; conc. H_2SO_4 converts it into anethoïn.

ANGELICA, OIL OF. The seeds of *Angelica archangelica* yield an essential oil (S.G. $\frac{0}{}$ ·872; $[\alpha]_D$ 13° 8′) containing a terpene, $C_{10}H_{16}$, (175°), S.G. $\frac{0}{}$ ·833, $[\alpha]_D = 12°$ 38′. The rotatory power of this terpene is reduced to 4° 52′ by heating for 432 hours at 100°; it is readily polymerised and easily oxidised (Naudin, *C. R.* 93, 1146). The essential oil also contains methyl-ethyl-acetic and oxymyristic acids (R. Müller, *B.* 14, 2476). The roots of *Angelica archangelica* yield an essential oil (S.G. $\frac{0}{}$ ·875) containing a terpene (166°), S.G. $\frac{0}{}$ ·870, $[\alpha] = 2°$ 50′. This terpene polymerises readily under the influence of heat or sodium (Naudin, *C. R.* 96, 1152; *Bl.* [2] 39, 406).

ANGELIC ACID $C_5H_8O_2$ *i.e.* $CH_2:CH.CH(CH_3).CO_2H$. *Pentenoic acid.* Mol. w. 100. [45°]. (185° i.V.).

Occurrence. — In the root of *Angelica archangelica* (Buchner, *A.* 42, 226). Oil of chamomile (*Anthemis nobilis*) may be separated by fractionating into isobutyl isobutyrate, isobutyl angelate, amyl angelate, and amyl tiglate; the residue contains hexyl tiglate and anthemol, $C_{10}H_{16}O$ (Köbig, *A.* 195, 95). Angelic acid is formed, together with laserol by heating laserpitin with alcoholic KOH (Feldmann, *A.* 135, 236).

Preparation.—1. Angelica root (50 lbs.) is boiled with lime (4 lbs.) and water, and the filtrate acidified with H_2SO_4 and distilled (Meyer a. Zenner, *A.* 55, 317).—2. Oil of chamomile is saponified by alcoholic KOH (Kopp, *A.* 195, 81; Pagenstecher, *A.* 195, 108; Beilstein a. Wiegand, *B.* 17, 2261).—3. Sumbul or moschus root contains a resin which when boiled with alcoholic KOH yields angelic and methyl-crotonic acids (Reinsch, *Jahrb. pr. Pharm.* 7, 79; E. Schmidt, *Ar. Ph.* [3] 24, 528).

Properties.—Monoclinic prisms or needles; sl. sol. cold water, v. sol. hot water, alcohol, and ether.

Reactions.—1. *Hydriodic acid* at 190° reduces it to valeric acid (Ascher, *Z.* [2] 6, 217).—2. *Potash-fusion* produces acetate and propionate (Demarçay, *C. R.* 80. 1400).—3. *Bromine* forms a dibromide [86°].—4. Conc. H_2SO_4 converts it into tiglic acid.—5. $KMnO_4$ gives CO_2 and aldehyde (B. a. W.).

Salts. — $BaA'_2 4\frac{1}{2}$aq: crystalline mass. — CaA'_2 2aq: long needles, much more soluble in cold, than in hot, water. — AgA′: feathery crystals, sl. sol. water.—PbA'_2: crystals, sl. sol. water.

Ethyl-ether.—EtA′. (141·5°). S.G. $\frac{0}{}$ ·935.

Isobutyl ether C_4H_9A'. (177°).

Isoamyl ether $C_5H_{11}A'$. (201°).

Anhydride $(C_5H_7O)_2O$. Oil (Chiozza, *A. Ch.* [3] 39, 210).

Hydriodide $CH_3.CHI.CH(CH_3).CO_2H$. [46°]. *Iodo-valeric acid.* Prisms. Formed by very conc. HI.

Constitution.—Angelic acid is isomeric with

allyl-acetic acid, CH_2:CH.CH_2.CH_2.CO_2H, methyl-crotonic or tiglic acid CH_3.CH:C(CH_3).CO_2H, β-β-di-methyl-acrylic acid $(CH_3)_2$C:CH.CO_2H (Ustinoff, *J. pr.* [2] 34, 484), propylidene-acetic acid, CH_3.CH_2.CH:CH.CO_2H, and tetra-methylene carboxylic acid.

The same valeric acid, (173°-175° uncor.), S.G. ^{15} ·941, is formed by reducing the hydriodides of angelic and of tiglic acids by Zn and H_2SO_4. It is probably CH_3.CH_2.CH(CH_3).CO_2H (Schmidt, *B.* 12, 252). Angelic acid changes when long kept, or when treated with $AgNO_3$, into tiglic acid, and hence the two acids have probably the same carbon skeleton. The hydriodide of angelic acid is, however, different from that of tiglic acid, CH_3.CH_2.CI(CH_3).CO_2H. This would be explained by assigning to angelic acid the formula CH_2:CH.CH(CH_3).CO_2H, its compound with HI being CH_3.CHI.CH(CH_3).CO_2H. The latter iodo-valeric acid is not CH_2I.CH_2.CH(CH_3).CO_2H for it gives no lactone on neutralisation with Na_2CO_3, but butylene CH_3.CH:CH.CH_3 (Fittig, *A.* 216, 161). An alternative formula, CH_2:CEt.CO_2H, would form with HI either CH_2I.CHEt.CO_2H or, more probably, CH_3.CIEt.CO_2H; sodium carbonate would convert the latter into an oxy-acid, or back into angelic acid, while the former would give the butylene CH_2:CH.CH_2.CH_3.

ANGELICO-BENZOIC OXIDE $C_{12}H_{12}O_3$ *i.e.* C_5H_7O.O.Bz. From potassium angelate and BzCl (Chiozza, *A.* 86, 260). Oil.

ANGELICO LACTONES. $C_5H_6O_2$. β-acetyl-propionic (levulic) acid splits up on distillation into H_2O and a mixture of these lactones, transition compounds being doubtless the two isomeric oxy-acids CH_3.C(OH):CH.CH_2.CO_2H and CH_2:C(OH).CH_2.CH_2.CO_2H. They are dried over K_2CO_3 and separated by fractional distillation (Wolff, *A.* 229, 249; *B.* 20, 425). The (α) lactone is converted into the (β) modification by combining it with HCl and distilling the product. Both lactones combine with bromine, and both are changed to β-acetyl-propionic acid by boiling with water or by treatment with cold aqueous baryta. This reaction is easily explained, for the oxy-acids CH_3.C(OH):CH.CH_2.CO_2H and CH_2:C(OH).CH_2.CH_2.CO_2H into which the lactones should be converted, would both change (by Erlenmeyer's rule) into CH_3.CO.CH_2.CH_2.CO_2H.

(α)-*Angelico-lactone* CH_3.C:CH.CH_2.CO.O (ring closed from C to O)

[18°]. (168°). V.D. 3·6. S. 5 at 15°. Is also formed by the action of water on the bromide of β-bromo-β-acetyl-propionic acid. Colourless neutral liquid, gradually turns yellow. It has a pleasant odour and bitter taste. At 0° it solidifies to white needles which are not hygroscopic and are volatile. The lactone dissolves in most solvents. It is separated by K_2CO_3 from its aqueous solution. If left a few hours with cold water the liquid becomes acid.

Reactions.—1. NH_3 converts it into β-acetyl-propion-amide.—2. Combines with bromine in CS_2 forming the lactone of di-bromo-oxy-valeric acid (*q. v.*).—3. Combines with HCl forming the lactone of chloro-oxy-valeric acid (*q. v.*).

(β)-*Angelico-lactone* CH_2:C.CH_2.CH_2.CO.O.

(209°) at 750 mm. (84°) at 25 mm. S.G. $\frac{0}{0}$ 1·1084. Colourless neutral liquid. It does not solidify at −15°. It is partly converted into its (α) isomeride every time it is distilled under atmospheric pressure. Miscible with water, has a pleasant odour. May be left for 4 hours with cold water without production of an acid.

Reactions.—1. Boiled with water it is very slowly converted into levulic acid.—2. Combines with bromine in CS_2.—3. Does not combine with HCl.

ANGELYL. The radicle C_5H_7O. Also applied by Hofmann to monovalent PENTENYL (*q. v.*).

ANGUSTURA OIL $C_{13}H_{24}O$. (266°). S.G. ·93. Obtained by distilling true Angustura bark (*Cusparia febrifuga*) with steam (Herzog, *J.* 1858, 444). The bark contains also cusparine and gasipeïne (*q. v.*).

ANHYDRIDES.—*Oxides which react with water to form acids* (*q. v.*), *or are obtained from acids by withdrawing water, or which react with basic oxides to produce salts: e.g.*

$SO_3 + H_2O = H_2SO_4$; $2HNO_3 - H_2O = N_2O_5$;
$SO_3 + BaO = BaSO_4$; $CrO_3 + BaO = BaCrO_4$.

Solutions of anhydrides in ether or other liquid quite free from water do not exhibit an acid reaction towards litmus. The greater number of the oxides of non-metals are anhydrides; the metallic oxides which belong to this class are usually those containing the greatest quantity of oxygen relatively to the metal. The more negative the character of an element the more do the lower oxides of that element exhibit the properties of anhydrides; the most positive elements do not form anhydrides. Metallic anhydrides do not, as a rule, produce acids by reacting with water, but most of them may be obtained from the corresponding hydrated oxides, having feebly-marked acid characters, by the action of heat; *e.g.* Nb_2O_5, PtO, PtO_2, TiO_2, SnO_2, &c. The formation of salts from these anhydrides is usually accomplished by fusing them with more basic oxides or hydrates; *e.g.* $Ta_2O_5 + K_2O$ (fused) $= K_2Ta_2O_6$; in some cases the metallic anhydride dissolves in strong aqueous potash or soda to form a salt; *e.g.* $Au_2O_3 + 2KOHAq = K_2Au_2O_4Aq + H_2O$. A definite connexion can be traced between the position of an element in the classificatory scheme founded on the periodic law and the existence or non-existence of anhydrides containing that element (*v.* OXIDES; also CLASSIFICATION; and PERIODIC LAW).

As a broad rule the anhydrides of the polybasic acids may be obtained from these acids by the action of heat (the anhydrides are usually the final products, before they are reached new acids are produced), but this rule has exceptions; *e.g.*, P_2O_5 cannot be obtained by heating H_3PO_4. The anhydrides of monobasic acids are usually obtained indirectly, often by the action of an acid chloride on a salt, *e.g.* $ClCl + HgClO = HgCl + Cl_2O$ (this method is largely used in preparing organic anhydrides, *v. next article*); these anhydrides are sometimes obtained from their acids by withdrawing water by the action of dehydrating agents; *e.g.* $2HNO_3 + P_2O_5 = N_2O_5 + P_2O_5H_2O$. A few anhydrides are produced by heating salts of the corresponding acids; *e.g.* $FeSO_4$ when heated in air forms $Fe_2S_2O_9$ and this on further heating gives Fe_2O_3 and $2SO_3$.

Besides their characteristic reactions with water and basic oxides, many anhydrides combine

with normal salts to produce 'acid' salts (v. SALTS); *e.g.* $K_2CrO_4 + CrO_3 = K_2Cr_2O_7$, $K_2WO_4 + WO_3 = K_2W_2O_7$. Many of the non-metallic anhydrides combine with their own or other acids to form new acids; *e.g.* the following compounds are thus produced, $(HNO_3)_2N_2O_5$, $H_2SO_4SO_3$, $HClSO_3$, HSO_3NO_2, &c. A few anhydrides react with basic oxides to form salts not of their own but of other acids; *e.g.*, N_2O reacts with Na_2O_2Aq to produce $NaNO_2Aq$ (not NaNO); such anhydrides seem to be obtainable, indirectly, from more than one acid, thus N_2O is got by heating HNOAq or by heating solid NH_4NO_3.

Most anhydrides may be regarded as constituted of two or more acid radicles united by oxygen atoms; on this view such formulæ as these would be applicable:—$NO_2.O.O_2N$; Cl.O.Cl, &c. The mutual relations between acids and anhydrides are repeated to a great extent in the relations of basic hydrates, or hydroxides, to their oxides; *e.g.* $Fe_2O_6H_6$ when heated yields $3H_2O$ and Fe_2O_3; CaO when added to H_2O produces CaO_2H_2, &c.

At one time the name anhydride included both base-producing and acid-producing oxides; then the former class was distinguished as basic-anhydrides; but now the name is almost universally employed with the meanings given to it in this article. The following are the best marked anhydrides containing metals:—Sb_2O_3, Sb_2O_5; As_2O_3, As_2O_5; (? Bi_2O_5); CrO_3; (? Di_2O_5); Au_2O_3; Ir_2O_3; PbO_2; MnO_2; MoO_3; Nb_2O_5; OsO_4; PtO, PtO_2; Ta_2O_5; SnO, SnO_2; TiO_2; WO_3; UO_3; V_2O_4, V_2O_5; ZrO_2. The sulphides, or hydrosulphides, of certain elements react with the anhydrides of thio-acids; *e.g.* As_2S_3 dissolves in KHSAq to form $KAsS_2Aq$, but the acid corresponding to this thio-arsenite is unknown; again, WS_3 dissolves in KHSAq to form K_2WS_4Aq, which reacts as the potassium salt of thio-tungstic acid (H_2WS_4), which acid has not itself been prepared. The thio-acid corresponding to the thio-anhydride SnS_2, viz. H_2SnS_3, has been prepared; CS_2 again is the thio-anhydride of thio-carbonic acid H_2CS_3. It is not, however, customary to apply the term anhydride to any sulphides even when an acid, or a series of salts, can be obtained from them. M. M. P. M.

ANHYDRIDES, ORGANIC.—The anhydride of an organic substance is a body derived from it by elimination of water. The water may be derived from one molecule, or several molecules may become united in the process; in the latter case 'condensation' is said to take place - a term which is also used when closed chains are produced. A molecule of water may be derived:

A. From two carboxyls.
B. From one carboxyl and one hydroxyl.
C. From two hydroxyls.
D. From one hydrogen and one hydroxyl.
E. From carboxyl and amidogen.
F. From carbonyl and amidogen.
G. From hydroxyl and amidogen.

A. FROM TWO CARBOXYLS.

Acid Anhydrides.

Formation.—1. On application of heat most monocarboxylic acids distil undecomposed, while di-carboxylic acids in which the carboxyls are attached to adjacent atoms of carbon give anhydrides, *e.g.*

$C_6H_4<^{CO.OH}_{CO.OH} = C_6H_4<^{CO}_{CO}>O + H_2O$. When the carboxyls are attached to the same atom of carbon, CO_2 is split off:

$$CH_3.CH(CO_2H)_2 = CH_3.CH_2.CO_2H + CO_2.$$

2. Anhydrides of monobasic acids are got by the action of acid chlorides on alkaline salts (Gerhardt, *A. Ch.* [3] 37, 285). Mixed anhydrides of monobasic acids may be got in the same way. Instead of the alkaline salt the free acid may be used (Linnemann, *A.* 161, 169). An acid heated with its chloride gives its anhydride in the following cases amongst others: acetic, trichloro-acetic, butyric, benzoic, and succinic acids. Acetyl chloride heated with dibasic acids gives anhydrides of the dibasic acid in the following cases amongst others (a mixed anhydride is perhaps first formed): succinic, chloro-succinic, bromo-succinic, maleïc, acetyl-malic, diacetyl tartaric, diacetyl racemic, citraconic, itaconic, camphoric, phthalic and diphenic acids. These anhydrides of dibasic acids readily absorb water from the air forming the corresponding hydrates, from which, however, they may be separated by chloroform which dissolves the anhydrides only. Benzoyl chloride acts like acetyl chloride. In neither case are mixed anhydrides formed.

Acetic anhydride at 120°-150° also converts dibasic acids into their anhydrides, *e.g.*: succinic, camphoric, phthalic, and diphenic acids (Anschütz, *A.* 226, 12).

3. Anhydrides are also formed by the action of lead nitrate on acid chlorides (Lachowicz, *B.* 17, 1281), *e.g.*:

$$2AcCl + Pb(NO_3)_2 = Ac_2O + PbCl_2 + N_2O_5.$$

4. By passing phosgene over heated salts (Hentschel, *B.* 17, 1285):

$$2NaOAc + COCl_2 = Ac_2O + 2NaCl + CO_2.$$

5. By warming the chlorides of the acids with dry oxalic acid, *e.g.* $2Ph.COCl + H_2C_2O_4 = (Ph.CO)_2O + 2HCl + CO_2 + CO$ (Anschütz, *A.* 226, 14).

Reactions.—1. Simple anhydrides may usually be *distilled* or sublimed, but mixed anhydrides such as BzOAc are split up by heat into two simple ones: $2BzOAc = Bz_2O + Ac_2O$.—2. They are insoluble in *water*, but slowly converted by it into the corresponding acid; a conversion that is more rapidly effected by alkalis.—3. *Alcohol* forms ethyl ethers of the corresponding acids.—4. *Ammonia* forms an amide and an ammonium salt: $Ac_2O + 2NH_3 = AcNH_2 + AcONH_4$, or, in the case of anhydrides of dicarboxylic acids, an amic acid.—5. *Sodium-amalgam* reduces them to aldehydes and alcohols (Linnemann, *A.* 148, 249).—6. PCl_5 forms $POCl_3$ and acid chlorides.—7. Heated with NaOAc in sealed tubes at 200° some anhydrides yield ketones (Perkin, *C. J.* 49, 325):

$$CH_3.CO_2Na + (CH_3CO)_2O = CH_3.CO.CH_3 + CO_2 + CH_3.CO_2Na.$$

$$CH_3.CO_2Na + (C_3H_7CO)_2O = C_3H_7.CO.CH_3 + CO_2 + C_3H_7.CO_2Na.$$

Intermediate addition-products, such as $CH_3.C(O.CO.C_3H_7)_2.ONa$, are perhaps the cause of this reaction.

B. FROM HYDROXYL AND CARBOXYL.

This is the ordinary process of etherification:

$$EtOH + CH_3.CO_2H = H_2O + CH_3.CO.OEt.$$

When hydroxyl and carboxyl are both present in the same molecule, spontaneous etherification may take place, the reaction taking place between two molecules, as in the formation of lactide, $O<\begin{matrix}CHMe.CO\\CO.CHMe\end{matrix}>O$, from lactic acid $HO.CHMe.CO_2H$, or by splitting off water from one molecule, *e.g.*

$$CH_3.CH(OH).CH_2.CH_2.CO_2H = CH_3.CH.CH_2.CH_2.CO.O.$$

In the latter case the alcoholic part of the molecule etherifies the acid part, and the product is called a lactone (*v.* LACTONES). Hydroxyl in the γ and δ positions gives rise to lactones.

C. FROM TWO HYDROXYLS.

The elimination of water between two hydroxyls in different molecules produces an oxide or simple ether. The result is brought about by first forming an intermediate compound, *e.g.*:

$EtOH + H_2SO_4 = EtO.SO_3H + H_2O$

$EtO.SO_3H + EtOH = EtOEt + H_2SO_4$ (*v.* ETHER).

When two hydroxyls are attached to one atom of carbon they usually split off water spontaneously, producing carbonyl.

Two hydroxyls attached to contiguous atoms of carbon may give rise to an oxide or internal ether, an intermediate body being first prepared, *e.g.*

$$HO.CH_2.CH_2OH + HCl = Cl.CH_2.CH_2OH + H_2O$$
$$Cl.CH_2.CH_2OH + KHO = \underbrace{CH_2.CH_2}_{O} + KCl + H_2O.$$

D. FROM ONE HYDROGEN AND ONE HYDROXYL.

Water can be eliminated by the union of hydroxyl with hydrogen when they are attached to adjacent atoms of carbon. This readily occurs with β-oxy acids, *e.g.*:

$$CH_2(OH).CH_2.CO_2H = H_2O + CH_2:CH.CO_2H.$$
$$C_6H_5.CH(OH).CH_2.CO_2H = H_2O + C_6H_5.CH:CH.CO_2H.$$

E. FROM CARBOXYL AND AMIDOGEN.

Water can be formed either from the hydroxyl and hydrogen, *e.g.*

$$C_6H_4<\begin{matrix}CO.CO.OH\\NH_2\end{matrix} = H_2O + C_6H_4<\begin{matrix}CO\\NH\end{matrix}>CO$$

or from the oxygen of the carbonyl and hydrogen:

$$C_6H_4<\begin{matrix}CO.CO.OH\\NH_2\end{matrix} = H_2O + C_6H_4<\begin{matrix}CO\\N\end{matrix}>C.OH.$$

Compounds resulting from the first mode of dehydration are called l a c t a m s, those resulting from the second mode of dehydration being termed l a c t i m s.

It is very difficult to say which formula best represents a given compound; Baeyer considers that the arrangement represented by the lactim is the more stable, but that before undergoing chemical reactions it usually changes to the transition or labile condition represented by the lactam. The prefix *pseudo* is frequently applied to distinguish a lactam from a lactim. In the aromatic series the elimination of water takes place spontaneously when the two side-chains are in the ortho position, and when the condensation can produce a ring, containing 5 or 6 atoms.

Thus $C_6H_4<\begin{matrix}CH:CH.CO_2H\\NH_2\end{matrix}$ condenses to $C_6H_4<\begin{matrix}CH:CH\\N\end{matrix}>C.OH$ while $C_6H_4<\begin{matrix}CH_2.CH_2.CH_2.CO_2H\\NH_2\end{matrix}$ does not produce an anhydride.

F. FROM CARBONYL AND AMIDOGEN.

The case in which carbonyl forms part of carboxyl has already been mentioned.

Mono-alkoyl-*o*-diamines and *o*-amido-alkoyl-phenols exhibit a tendency to split off water and form *Anhydro compounds*, *e.g.*

$$C_6H_4<\begin{matrix}NH.CO.CH_3\\NH_2\end{matrix} = H_2O + C_6H_4<\begin{matrix}NH\\N\end{matrix}>C.CH_3$$
$$C_6H_4<\begin{matrix}O.CO.C_6H_5\\NH_2\end{matrix} = H_2O + C_6H_4<\begin{matrix}O\\N\end{matrix}>C.C_6H_5$$

(Hübner, *A.* 208, 278; 209, 339; 210, 328). The first class of compounds may be viewed as amidines. These anhydro-compounds are formed: (1) From aromatic alkoylamides or alkyl phenols by nitration and reduction with tin and glacial acetic acid. (2) From [1:2] amido- (or oxy) nitro-compounds by heating with acid chlorides or anhydrides, and reducing the product. (3) From *o*-diamines or *o*-amido-phenols by heating with acid chlorides or anhydrides.

G. FROM HYDROXYL AND AMIDOGEN.

Alkyls can be introduced into amidogen by heating an amine with an alcohol or phenol, especially in presence of dehydrating agents: thus aniline boiled with (β)-naphthol gives phenyl-(β)-naphthylamine.

ANHYDRO-ACET-DI-AMIDO-BENZENE *v.* ETHENYL-PHENYLENE-DIAMINE.

ANHYDRO - ACET - DI - AMIDO - BENZOIC ACID *v.* ETHENYL-DI-AMIDO-BENZOIC ACID.

ANHYDRO-ACETYL- *v.* ETHENYL-.

ANHYDRO-DI-ACETYL-ACETAMIDIL *v.* ACETAMIDINE.

ANHYDRO-DI-ACETYL-ACETAMIDINE *v.* ACETAMIDINE.

ANHYDRO - o - AMIDO - PHENOL - ACETO - ACETIC ETHER *v.* PROPENYL-*o*-AMIDO-PHENOL ω-CARBOXYLIC ETHER.

ANHYDRO - AMIDO - PHENOXY - ACETIC ACID *v.* GLYCOLLIC ACID.

ANHYDRO-AMIDO-TOLYL-OXAMIC ACID *v.* DI-OXY-METHYLQUINOXALINE.

ANHYDRO-ATROPINE *v.* ATROPYL-TROPEÏN.

ANHYDRO-BENZ- *v.* BENZENYL-.

ANHYDRO-BENZ-DIAMIDO-BENZENE *v.* BENZENYL-PHENYLENE-DIAMINE.

ANHYDRO-BENZ - DIAMIDO - TOLUENE *v.* BENZENYL-TOLYLENE-DIAMINE.

ANHYDRO-BENZ-DI-AMIDO-TOLUIC ACID *v.* BENZENYL-PHENYLENE-DIAMINE CARBOXYLIC ACID.

ANHYDRO-BENZOYL- *v.* BENZENYL-; or named as derivatives of benzamidine.

ANHYDRO - BENZOYL - AMIDO-DI - TOLYL-AMINE *v.* BENZENYL-TOLYL-TOLYLENE-DIAMINE.

ANHYDRO - CHLORO - FORMYL - AMIDO - PHENYL MERCAPTAN *v.* CHLORO-METHENYL-AMIDO-PHENYL MERCAPTAN.

ANHYDRO-CINNAMOYL- *v.* CINNAMENYL-.

ANHYDRO-TRI-ETHYL-SULPHAMIC ACID *v.* *Tri*-ETHYL-AMINE.

ANHYDRO-FORMYL- *v.* METHENYL- or named as derivatives of formamidine.

ANHYDRO-GLYCOLYL- *v.* OXY-ETHENYL-.

ANHYDRO-LUPININE *v.* LUPININE.

ANHYDRO-NAPHTHOL SULPHONIC ACID *v.* NAPHTHOL-SULPHONIC ACID.

ANHYDRO - OXALYL - AMIDO - PHENYL MERCAPTAN $C_{14}H_8N_2S_2$ *i.e.*

$C_6H_4\left\langle{N \atop S}\right\rangle C-C\left\langle{N \atop S}\right\rangle C_6H_4$. [about 300°].

Formation.—1. By heating amido-phenyl mercaptan with oxalic acid and PCl_3.—2. By the action of the chloro-methenyl-amido-phenyl mercaptan on methenyl-amido-phenyl mercaptan.—3. By heating chloro-methenyl-amido-phenyl mercaptan with zinc.—4. By the action of acetyl chloride or benzoyl chloride at 150° on methenyl-amido-phenyl mercaptan.

Preparation.—1. By heating acetanilide (5 pts.) with sulphur (3 pts.) to boiling for 30 hours; yield 25 to 30 p.c.—2. By leading $(CN)_2$ gas into an alcoholic solution of amido-phenyl mercaptan.

Properties.—Sublimable. Colourless glistening plates. Nearly insoluble in all solvents; dissolves best in toluene. Bitter taste.

Reactions.—By fusing with KOH at 200° it is readily split up into amido-phenyl mercaptan and oxalic acid. On reduction with HI and P at 150° it gives aniline and ethenyl-amido-phenyl mercaptan (Hofmann, *B.* 13, 1226).

ANHYDRO - OXALYL - DI - PHENYLENE - TETRA-AMINE $C_{14}H_{10}N_4$ *i.e.*

$C_6H_4\left\langle{N \atop NH}\right\rangle C.C\left\langle{N \atop NH}\right\rangle C_6H_4$. [above 300°]. From *o*-di-nitro-oxanilide, Sn, and glacial HOAc (Hübner, *A.* 209, 370). Yellow needles; insol. water, CS_2, and light petroleum, m. sol. glacial HOAc, sl. sol. alcohol, ether and benzene.

Salts.—$B''2HCl$ 2aq.—$B''H_2SO_4$ 2aq.

ANHYDRO-OXALYL-DI-TOLYLENE-TETRA-AMINE

$C_6H_3(CH_3)\left\langle{N \atop NH}\right\rangle C-C\left\langle{N \atop NH}\right\rangle C_6H_3(CH_3)$.

[193°?]. Formed by heating oxalyl-di-tolylene-diamine to above 200° (Hinsberg, *B.* 15, 2691). Or from di-nitro-di-tolyl-oxamide, Sn, and HCl (Hübner, *A.* 209, 373).

Salts.—$B''H_2Cl_2$.—$B''(AcOH)_2$: glistening plates.—$B''_2H_2SO_4$ 4aq: needles.

ANHYDRO-PHENYL-ACETYL- *v.* PHENYL-ETHENYL-.

ANHYDRO - PHTHALYL - AMIDO-PHENYL MERCAPTAN $C_{20}H_{12}N_2S_2$ *i.e.*

$C_6H_4\left\langle{N \atop S}\right\rangle C-C_6H_4-C\left\langle{N \atop S}\right\rangle C_6H_4$. [112°].

Prisms or needles. Insol. water, sol. alcohol. Weak base. Prepared by heating amido-phenyl mercaptan hydrochloride with phthalyl chloride. Salts.—$B'HCl$: decomposed by water $(B'HCl)_2PtCl_4$: slender needles (Hofmann, *B.* 13, 1233).

ANHYDRO-PROPIONYL- *v.* PROPENYL-.

ANHYDRO-PYROGALLO-KETONE *v.* *Hexa-*OXY-BENZOPHENONE.

ANHYDRO-SALICYL- *v.* OXY-BENZENYL-.

ANHYDRO - SUCCINYL - AMIDO - PHENYL MERCAPTAN $C_{16}H_{12}N_2S_2$ *i.e.*

$C_6H_4\left\langle{N \atop S}\right\rangle C.CH_2.CH_2.C\left\langle{N \atop S}\right\rangle C_6H_4$. [137°].

Prepared by the action of succinamide on amido-phenyl mercaptan. Colourless needles. Dissolves in acids forming unstable salts. Very stable towards reducing agents. By fusing with KOH amido-phenyl mercaptan is reproduced. Salts.—$B'HCl$: yellow needles, decomposed by water.—$(B'HCl)_2PtCl_4$: sparingly soluble spangles.—$B'HClAuCl_3$: yellow needles (Hofmann, *B.* 13, 1231).

ANHYDRO-SULPHAMIDO- *v.* SULPHO-.

ANHYDRO - TOLUYL - DI - AMIDO - BENZENE *v.* TOLUENYL-PHENYLENE-DIAMINE.

ANHYDRO-TOLUYL-DIAMIDO-TOLUENE *v.* TOLUENYL-TOLYLENE-DIAMINE.

ANHYDRO-VALERYL- *v.* PENTENYL-.

ANIL- *v.* PHENYL-IMIDO-.

ANIL - ACETOACETIC ACID *v.* p. 19, *Reaction* 18.

ANIL-BENZYL-MALONIC ETHER $C_{20}H_{21}NO_4$ *i.e.* $C_6H_5.N:C(C_6H_5).CH(CO_2Et)_2$. [75°]. Formed by the action of *exo*-chloro-benzylidene-aniline $C_6H_5.CCl:NPh$ upon sodio-malonic ether (Just, *B.* 18, 2624). Large crystals; v. sol. alcohol and ether, insol. water. It contains a hydrogen atom readily displaceable by sodium. Heated with dilute HCl at 120° it is split up into acetophenone, aniline, ethyl chloride, and CO_2. By heating alone to about 150° it eliminates alcohol and is converted into (*Py.* 1:3:2)-oxy-phenyl-quinoline-carboxylic ether

$$C_6H_4\begin{cases} C(OH):C.CO_2Et. \\ N\text{——}CPh. \end{cases}$$

Di-anil-benzyl-malonic ether $C_{33}H_{30}N_2O_4$ *i.e.* $(PhN:CPh)_2C(CO_2Et)_2$. Formed by the action of *exo*-chloro-benzylidene-aniline upon the sodium compound of mono-anil-benzyl-malonic ether (J.). Plates. By heating with dilute HCl or H_2SO_4 at 120° it is split up into benzoic acid, aniline, acetic acid, ethyl chloride, and CO_2.

ANILIDES.—Substances derived from acids by displacement of the hydroxyl by phenyl-amidogen (NHPh). They are usually described under the acids to which they belong. The term anilide may also be applied more generally to phenyl-amides and phenyl-imides.

Anilides of acids.

Formation.—1. From aniline and acid chlorides: $C_6H_5COCl + NPhH_2 = HCl + C_6H_5CO.NPhH$. 2. By boiling amides with the equivalent quantity of aniline until no more NH_3 comes off, and purifying by washing with ether (Kelbe, *B.* 16, 1199). $X.CO.NH_2 + NPhH_2 = X.CO.NPhH + NH_3$. 3. In some cases, *e.g.* formic and acetic acids, anilides are formed by simply heating aniline with the dry acid (*cf.* Tobias, *B.* 15, 2866).—4. By action of aniline upon compound ethers.—5. By the action of aniline on acid anhydrides.

Properties.—Solid crystalline substances, v. sl. sol. water.

Reactions.—Split up into acid and aniline by boiling aqueous or alcoholic KOH, by heating with HCl in a sealed tube, or by heating with conc. H_2SO_4 at 100°.

Anilides of phosphorous acid.

Tri-anilide $P(NHPh)_3$ *v.* ANILINE, *react.* 29.

Di-anilide $P(NHPh)_2(OH)$. Prepared by heating a mixture of aniline (3 pts.) and PCl_3 (1 pt.), extracting with ether and ppg. with water (Jackson a. Menke, *Am.* 6, 89). White amorphous mass; sol. alcohol and ether.

Anilides of phosphoric acid.

Tri-anilide $PO(NHPh)_3$. [208°]. From aniline and $POCl_3$ (Schiff, *A.* 101, 302; Michaelis a. Soden, *A.* 229, 335). Thin needles or six-sided trimetric plates (from alcohol). Insol. water, aqueous acids, or alkalis. Forms a hexa-bromo derivative, [258°].

Di-anilide $PO(OH)(NHPh)_2$. [197°]. From aniline (2 pts.) and $POCl_3$ (1 pt.), the product being treated with water (M. a. S.). Insol. water. Saponified by water or acids, not by alkalis.

Anilide of thio-phosphoric acid $PS(NHPh)_3$. [78°]. From $PSCl_3$ and aniline (Chevrier, *Z.* 1868, 539). Insol. water.

Anilide of arsenic acid $AsO(OH)_2(NHPh)$. Formed by heating aniline arsenate (Béchamp, *C. R.* 56, 1172).

Anilide of boric acid $B_2O_3NPhH_2$(?). From ethyl borate and aniline. Decomposed by water (Schiff, *A. Suppl.* 5, 209).

ANILIDO- *v.* PHENYL-AMIDO-.

ANILINE C_6H_7N *i.e.* $C_6H_5NH_2$. *Phenylamine.* Mol. w. 93. [−8°] (Lucius, *B.* 5, 154). (185° cor.). (*Private communication from* R. J. Friswell); (183·7°) (Thorpe, *C. J.* 37, 221). S.G. $\frac{0}{4}$ 1·0379 (T.). $\frac{20}{4}$ 1·0216 (Brühl); $\frac{15}{4}$ 1·0212 (Friswell). C.E. (0°–10°) ·000866; (0°–100°) ·000925 (T.). (14°–25°) ·000818 (F.). H.F.p. −17450 (Thomsen); 2747 (Ramsay). H.F.v. −19190 (Th.). μ_β 1·6043 (B.). R_∞ 49·83 (B.). S.V. 106·37 (T.); 106·08 (R. Schiff, *B.* 19, 566); 109·1 (Ramsay). *Vapour pressure*: Ramsay a. Young (*C. J.* 47, 647, 655). S. 5 at about 15°; the S.G. of the saturated aqueous solution is $\frac{15}{15}$ 1·0023; $\frac{21}{21}$ 1·001. 100 pts. of a solution of water in aniline at 8° contain 4·6 pts. water (W. Alexejeff, *B.* 10, 709). Aniline saturated with water has S.G. $\frac{15}{4}$ 1·025 (Friswell).

Formation.—1. Discovered by Unverdorben (*P.* 8, 397) among the products of distillation of indigo, and called by him *crystalline.*—2. Rediscovered in coal tar by Runge (*P.* 31, 65, 513; 32, 331) and called by him *cyanol.*—3. Obtained by distilling indigo (from *Indigofera 'Anil'*) with potash (Fritzsche, *J. pr.* 20, 453; 27, 153; 28, 202) and then first called *aniline.*—4. Obtained from nitro-benzene by reducing with ammonium sulphide by Zinin (*J. pr.* 27, 149; 36, 98) and called by him *benzidam.* Also obtained by reducing nitro-benzene with other agents: *e.g.* Zn and HCl (Hofmann, *A.* 55, 200), ferrous acetate (Béchamp, *A. Ch.* [3] 42, 186), aqueous As_2O_3 and NaOH (Wöhler, *A.* 102, 127), zinc dust and water (Kremer, *J. pr.* 90, 255).—5. In Dippel's animal oil (Anderson, *A.* 70, 32).—6. By dry distillation of amido-benzoic acids (Hofmann a. Muspratt, *A.* 53, 221).—7. By distilling isatin with potash (Hofmann, *A.* 53, 11).—8. From di-phenyl-urea or di-phenyl-thio-urea by action of P_2O_5, zinc chloride, or HCl (Hofmann, *Pr.* 9, 274): $CO(NPhH)_2 = NPhH_2 + CO{:}NPh$.—9. Among products of distillation of peat (Vohl, *J. Ph.* [3] 36, 319).—10. By heating potassium benzene sulphonate with sodamide ([illegible]son a. Wing, *B.* 19, 902).—11. By the action of Br in alkaline solution upon benzamide (Hofmann, *B.* 18, 2737).—12. From phenol, and NH_3.—(*a*) Together with diphenylamine by heating phenol with zinc-chloride-ammonia, $Zn(NH_3)_2Cl_2$, at 300° to 350°. The addition of NH_4Cl diminishes the quantity of diphenylamine and improves the yield of aniline. The best yields (c. 55 p.c. aniline and 15 p.c. diphenylamine) are obtained by heating 1 pt. of phenol with 4 pts. $Zn(NH_3)_2Cl_2$ and 4 pts. NH_4Cl under pressure at [illegible]0°–340° for 20 hours.—(*b*) Together with diphenylamine by heating phenol with a mixture of NH_4Cl and ZnO; also in this case an excess of NH_4Cl diminishes the quantity of secondary amine formed. The best yields (c. 55 p.c. aniline and 20 p.c. diphenylamine) are obtained by heating 2 pts. phenol with 2 pts. ZnO and 3 pts. NH_4Cl at c. 330° for 20 hours under pressure.—(*c*) About the same results are obtained by substituting $Zn(NH_3)_2Br_2$ NH_4Br for the chlorides in (*a*) and (*b*).—(*d*) Together with diphenylamine by heating phenol with NH_4Cl and MgO. A yield of 45 p.c. aniline and 20 p.c. diphenylamine was obtained by heating 20 pts. phenol with 8·8 pts. MgO and 24 pts. NH_4Cl for 40 hrs. at 340°–350°.—(*e*) Small quantities of aniline and diphenylamine (c. 4 p.c. aniline and 15 p.c. diphenylamine) are formed by heating phenol (1 pt.) with NH_4Cl (2 pts.) alone, at 370°–400° (Merz a. Müller, *B.* 19, 2901).—13. Diphenylamine heated with conc. HCl at 320° yields small quantities of aniline and phenol.

Preparation. — By reducing nitro-benzene with iron filings in presence of a small quantity of hydrochloric or acetic acid:

$$4PhNO_2 + 4H_2O + 9Fe = 4PhNH_2 + 3Fe_3O_4.$$

Nitrobenzene (100 pts.), water (40 pts.), iron borings (25 pts.), and HClAq (9 pts.) are mixed in a cast iron vessel and the reaction started by admission of steam; more iron borings (90 pts.) are then slowly added. When the reduction is complete, lime is added, and the aniline (67 pts.) distilled over with steam. Pure aniline is best prepared from pure benzene. Aniline may be purified by conversion into its acetyl derivative, recrystallising this from water, and saponifying it with alkalis or acids. Aniline phosphate is less readily soluble in water than *o*-toluidine phosphate (Lewy, *C. J.* 46, 46).

Properties.—Colourless oil; sl. sol. water, miscible with most other menstrua. Turns red in air. Soluble in aqueous solutions of aniline hydrochloride. Its aqueous solution does not change the colour of red litmus or yellow turmeric but it changes the violet colour of dahlia to green. Congo red may also be used as an indicator (Julius, *S. C. I.* 9, 109). Aniline pps. ferrous, ferric, aluminium, and zinc, hydrates from their salts; it forms double salts with $PtCl_4$, $AuCl_3$, $HgCl_2$, $SbCl_3$, and $SnCl_4$. It gives a brownish pp. with tannin. It coagulates albumen. Potash, soda, and lime expel aniline from its salts. NH_3 is expelled when aqueous ammonium salts are boiled with aniline, but aniline is liberated when NH_3 is added to cold aqueous solutions of its salts.

Detection.—1. Very dilute aqueous solutions give a violet colour with bleaching powder; the colour is destroyed by shaking with ether (Runge). 2. Extremely dilute aqueous solutions treated successively with bleaching powder and a drop of ammonium sulphide give a rose colour (Jacquemin, *Bl.* [2] 20, 68).—3. A solution of aniline in conc. H_2SO_4 mixed with a little solid $K_2Cr_2O_7$ gives after some time a splendid blue colour; the reaction is hastened by gently warming (Beissenhirz, *A.* 87, 376).—4. If a drop of $CuSO_4Aq$ is added to an aqueous solution of aniline an apple-green crystalline pp. is formed even if the solution is very dilute; in extremely dilute solutions a green coloration is produced (Friswell).

Reactions.—1. Aniline vapour passed through a *red-hot tube* forms C, NH_3, HCN, benzene, benzonitrile (Hofmann, *Pr.* 12, 383), carbazol (Graebe, *A.* 167, 125), iso-benzidine (*v.* DI-AMIDO-DIPHENYL), and quinoline (Bernthsen, *B.* 19, 420).

2. *Electric sparks* passed through liquid aniline form carbon, and a gas containing hydrogen (65 p.c.), acetylene (21 p.c.), prussic acid (9 p.c.), and nitrogen (5 p.c.) (Destrem, *C. R.* 99, 138).

3. Dilute H_2SO_4 and MnO_2 form NH_3 (Matthiessen, *Pr.* 9, 637), and a little quinone (Hofmann, *Pr.* 13, 4).

4. *Chromic acid*, CrO_3, sets fire to aniline.

5. *Chromic acid mixture* produces quinone.

6. *Potassium chlorate* and *hydrochloric acid* give tetrachloroquinone (chloranil) and trichlorophenol (Hofmann, *A.* 47, 67; 53, 28).

7. *Potassium permanganate* gives some azobenzene (Glaser, *A.* 142, 364), NH_3, and oxalic acid (Hoogewerff a. Dorp, *B.* 10, 1936; 11, 1202).

8. *Hydrogen peroxide* also produces azobenzene (Leeds, *B.* 14, 1384); which is also formed by passing aniline vapour over heated PbO (Behr a. Dorp, *B.* 6, 755).

9. *Potassium permanganate* in acid solution forms aniline black.

10. Strong *nitric acid* violently attacks aniline; picric acid is among the products. Aniline nitrate dissolved in a large quantity of H_2SO_4 produces *m*-nitro-aniline and a small quantity of *p*-nitro-aniline (Levinstein, *B.* 18, Ref. 203).

11. A mixture of aniline, *o-toluidine*, and *p-toluidine*, is converted by oxidising agents such as *nitric acid*, *mercuric chloride*, *lead nitrate*, *silver nitrate*, *arsenic acid*, and *stannic chloride* into aniline red (*v.* ROSANILINE).

12. *Nitrous acid* converts cold aqueous salts of aniline into salts of diazo-benzene (*v.* DI-AZO-COMPOUNDS); on boiling the solution nitrogen is evolved and phenol formed. Nitrous acid passed into a cold alcoholic solution of aniline produces diazo-benzene anilide.

13. When aniline is boiled with *sulphur* H_2S is evolved and di-amido-di-phenyl sulphide (thio-aniline) is formed together with other products of substitution of hydrogen by sulphur (Merz a. Weith, *B.* 3, 978).

14. *Potassium* produces NH_3 and azobenzene (Girard a. Caventou, *Bl.* [2] 28, 530).

15. *Chlorine* acts upon dry aniline with great violence, producing a black mass containing tri-chloro-aniline.

16. *Bromine* behaves like chlorine. *Bromine-water* added to solutions of salts of aniline gives a pp. of tri-bromo-aniline $C_6H_2Br_3NH_2$ [2:4:6:1]. Bromine has no action on a solution of aniline in conc. H_2SO_4 (Morley, *C. J.* 51, 582).

17. *Iodine* dissolves in aniline forming hydriodide of *p*-iodo-aniline.

18. Hot conc. *sulphuric acid* forms *p*-amido-benzene sulphonic acid; hot fuming H_2SO_4 forms amido-benzene disulphonic acid (Buckton a. Hofmann, *C. J.* 9, 260).

19. *Sulphide of carbon* forms di-phenyl thio-urea.

20. *Sulphide of carbon* and *ammonia* produce crystals of $C_{14}H_{18}N_4S_3$ or $(PhNH_2.NH.CS)_2S$, decomposed by boiling water into CS_2, NH_3, and di-phenyl-thio-urea (Hlasiwetz a. Kachler, *A.* 166, 142).

21. *Carbon tetrabromide* forms diphenyl-*p*-amido-benzamidine hydrobromide $PhNH.C(NPh).C_6H_4.NH_2HBr$ (Bolas a. Groves, *A.* 160, 174). CCl_4 acts similarly (Hofmann, *Pr.* 9, 284).

22. *Cyanogen* forms a 'cyan-aniline' $(C_6H_5NH_2)_2C_2N_2$, [210°–220°] (Hofmann, *A.* 66, 129; 73, 180; *B.* 3, 763). Insol. water, sl. sol. alcohol. Boiling acids decompose it into phenyl-oxamide, di-phenyl-oxamide, oxamide, aniline, and NH_3. Nitrous acid produces a base $C_{14}H_{15}N_5O_5$ (Senf, *J. pr.* [2] 31, 543). Salts of Cyananiline: $B''2HCl$. — $B''H_2PtCl_6$. — $B''2HAuCl_4$.—$B''2HBr$.—$B''2HNO_3$.

23. *Chloride of sulphur* diluted with CS_2 forms tri-phenyl-guanidine (di-phenyl thio-urea being first formed, Claus a. Krall, *B.* 3, 527; 4, 99).

24. Heated with *persulphocyanic acid* it gives phenyl-thio-biuret.

25. *Carbonyl chloride*, $COCl_2$, gives di-phenyl-urea.

26. *Gaseous cyanogen chloride* forms di-phenyl-guanidine (melaniline); in presence of water phenyl-urea is formed (Hofmann, *A.* [illegible] 70, 130). CyCl passed into an ethereal solution forms phenyl cyanamide (cyananilide, Cahours a. Cloëz, *C. R.* 38, 354). *Solid chloride of cyanogen* forms 'chlorocyananilide' $C_{15}H_{12}ClN_5O$ (Laurent, *A.* 60, 273).

27. *Cyanic acid* forms phenyl-urea.

28. When treated in ethereal solution with perchloromethylmercaptan $CCl_3.SCl$ it yields the compound $CCl_3.S.NHC_6H_5$. If the ethereal solution of the latter body is mixed with alcoholic KOH or NH_3 it splits off HCl and a crystalline compound separates which has the probable constitution $CCl_2.S.NC_6H_5$, (Rathke, [illegible] 19, 395).

29. *Phosphorus trichloride* acts [illegible] vigorously, producing 'phosphaniline hydrochloride' $PCl_3 3C_6H_7N$ (Tait, *Z.* [2] i., 649). [illegible] is perhaps the anilide of phosphorous acid $P(NPhH)_3 3HCl$. $PtCl_2PCl_3$ forms $(PhNH)_3PPtCl_2$ [illegible] $(K_2NH_2PhHCl$ whence water produces $(PhNH)$ [illegible] $N)_3PPtCl(OH)$ (Quesneville, *Monit. scient.* [3] [illegible] 6, 659). $PCl_3 2PtCl_2$, alcohol, and aniline [illegible] produce $P(OEt)_3PtCl_2(C_6H_7N)_2$ and $P_2(OEt)_6P$ [illegible] $Cl_2(C_6H_7N)_2$ (Cochin, *C. R.* 86, 1402).

30. *Phosphorus oxychloride* [illegible] produces very unstable anilide of phosphoric acid [illegible] $PO(NPhH)_3$ (Schiff, *A.* 101, 302; Michaelis a. S[illegible]oden, *A.* 229, 335).

31. Aniline, *isobutyric acid*, and $ZnCl_2$ give iso-butyric anilide (Bardwell, *Am.* [illegible], 116).

32. *Aniline-zinc-chloride* and *isoamyl alcohol* give amido-phenyl-isopentane.

33. *Chloroform* at 190° forms di-phenyl-formamidine, CH(NPh)(NPhH).

34. *Chlorides*, *bromides*, and *iodides* of alcoholic or acid radicles act upon aniline as they do upon other primary amines (*v.* AMINES). Alkyls may also be introduced by heating aniline hydrochloride or, better, hydrobromide with alcohols (Staedel a. Reinhardt, *B.* 1[illegible], 29). Methyl-aniline hydrochloride is converted by heat into toluidine hydrochloride (Hofmann, *B.* 5, 720); similarly aniline hydrochloride heated with MeOH at 290° forms $C_6H_4MeNMe_2$.

$C_6H_3Me_2NMe_2$, $C_6H_2Me_3NMe_2$, $C_6HMe_4NMe_2$, and C_6Me_5 (Hofmann a. Martius, *B.* 4, 742).

35. *Aldehydes* act upon aniline with elimination of water: *e.g.*

$CH_3.CHO + 2H_2NPh = H_2O + CH_3.CH(NHPh)_2$

$CH_3.CHO + H_2NPh = H_2O + CH_3.CH:NPh$

(Schiff, *A. Suppl.* 3, 344). The last formula ought perhaps to be written $(CH_3.CH)_2(NPh)_2$ (*v.* METHYLENE-ANILINE; ETHYLIDENE-ANILINE; CHLORO-ETHYLIDENE-ANILINE, &c.). Aniline acts similarly upon *glucose*, *levulose*, and *galactose*, forming $C_6H_7(OH)_5(NPh)$ (Schiff, *A.* 154, 30; Sorokin, *B.* 19, 513).

36. *Aniline sulphite* gives with an ethereal solution of *aldehyde* prisms of $PhNH_2C_2H_4OSO_2$ or $PhNH.SO_2.CHMe.OH$ (Schiff, *A.* 140, 127; 210, 129).

37. *Chloral* and aqueous SO_2 produce unstable crystals of $PhNH_3SO_3.CH(OH).CCl_3$ (Schiff, *A.* 210, 129).

38. *Acetone* and aqueous SO_2 form an unstable compound, $PhNH_2C_3H_6O\,SO_2$ which is perhaps $Me_2C(OH).SO_2.NHPh$ (S.).

39. *Acetone* (1 mol.) and P_2O_5 two days at 180° form $Me_2C:NPh$, (200°-220°) (Engler a. Heine, *B.* 6, 642; *cf.* Pauly, *A.* 187, 222).

40. Aniline hydrochloride heated with *acetone* or *mesityl oxide* at 190° forms some (*Py.* 1, 3)-di-methyl-quinoline (Engler a. Riehm, *B.* 18, 2245, 3296).

41. A mixture of *aldehyde* and *acetone* at 100° give (*Py.* 1, 3)-di-methyl-quinoline (Beyer, *J. pr.* [2] 33, 393).

42. *Paraldehyde* and conc. HCl at 100° form (*Py.* 3)-methyl-quinoline (quinaldine, Doebner a. von Miller, *B.* 16, 2464).

43. Aniline (1 pt.) distilled with *glycerin* (1 pt.) and H_2SO_4 (2 pts.) forms *quinoline* (Königs, *B.* 13, 911).* Quinoline is also formed by distilling acroleïn-aniline, or by heating aniline with *glycerin*, *nitrobenzene*, and H_2SO_4 (Skraup, *M.* 2, 141). *Aniline-zinc-chloride* heated with glycerin forms skatole (Fischer a. German, *B.* 16, 710).

44. *Aceto-acetic ether* at 120°-150° gives aceto-acetic anilide $CH_3.CO.CH_2.CO.NPhH$ (*cf.* ACETO-ACETIC ACID, *reaction* 18), [85°]. Sl. sol. water and NH_3Aq, v. sol. NaOHAq and acids. Distilled with aniline it gives *s*-di-phenyl urea. Boiling potash produces aniline, acetone, and acetic acid. Fe_2Cl_6 colours its aqueous solution violet. Br produces $CH_3.CO.CHBr.CONPhH$, [138°]. Conc. H_2SO_4 forms (*Py.* 3, 1)-oxy-methyl-quinoline. Nitrous acid forms $CH_3.CO.C(NOH).CO.NPhH$, [100°] (Knorr, *A.* 236, 75).

45. *Acetophenone cyanhydrin* gives rise to $C_6H_5.CMe(NHPh)CN$ (Jacoby, *B.* 19, 1515).

46. An alcoholic solution of *quinone* produces $C_6H_2(NHPh)_2O_2$ and hydroquinone. The former dissolves in conc. H_2SO_4 forming a crimson solution.

47. *Tetrachloro-quinone* (chloranil) produces, similarly, $C_6Cl_2(NHPh)_2O_2$ (Hofmann, *Pr.* 13, 4; Hesse, *A.* 114, 292; Knapp a. Schultz, *A.* 210, 164).

48. *Aniline* mixed with an *anilide* and PCl_3 produces a phenyl-amidine: *e.g.*

$3PhNH_2 + 3CH_3.CO.NHPh + 2PCl_3 =$
$3CH_3.C(NPh).NHPh + P_2O_3 + 6HCl$ (Hofmann, *Z.* 1866, 161).

49. *Aniline hydrochloride* and *acetonitrile* at 170° produce phenyl-acetamidine:
$CH_3CN + H_2NPh = CH_3C(NPh).NH_2$.

50. With *benzo-trichloride*, $PhCCl_3$ (1 mol.), aniline (2 mols.) on warming acts violently forming the hydrochloride of di-phenyl-benzamidine, $C_6H_5C(NPh)(NPhH)2HCl$: aniline in glacial acetic acid, $ZnCl_2$ and $PhCCl_3$ give, chiefly, the same body.

51. But aniline hydrochloride (40 pts.), *nitrobenzene* (45 pts.), *benzo-trichloride* (40 pts.), and *iron filings* at 180° form the chloride of di-amido-tri-phenyl-carbinol (*q. v.*).

52. Aniline (2 mol.) boiled with *chloro-acetic acid* (1 mol.) and *water* produces phenyl-amido-acetic acid and phenyl-imido-di-acetic acid; the aniline salt of the latter, $PhN(CH_2.CO_2NH_3Ph)_2$, crystallises in needles, [99°] (P. Meyer, *B.* 14, 1325).

53. An alcoholic solution of aniline, *chloro-acetic acid*, and *ammonium sulphocyanide* at 100° deposits crystals of phenyl-thio-hydantoïc acid $NH_2.C(NPh).S.CH_2.CO_2H$, [148°-152°]. This acid is decomposed by boiling with dilute (20 p.c.) H_2SO_4 into phenyl-urea and thio-glycollic acid (Jaeger, *J. pr.* [2] 16, 17; Claesson, *B.* 14, 732; Liebermann, *A.* 207, 129).

54. *Acetamidoxim hydrochloride* is converted by heating with aniline into acetanilidoxim, $CH_3.C(NOH).NHPh$, [121°] (Nordmann, *B.* 17, 2753).

55. *Zincethide* forms zinc anilide $Zn(NHPh)_2$, which is decomposed by water into $Zn(OH)_2$ and aniline (Frankland, *Pr.* 8, 504).

Salts.—(Beamer a. Clarke, *Am.* 1, 151; *B.* 12, 1066; Hjortdahl, *Z. K.* 6, 471). — B'HCl. [192°] (Pinner, *B.* 14, 1083). Needles or plates, v. sol. water and alcohol; may be sublimed.— $B'_2H_2PtCl_6$: yellow needles. — $B'_2H_2SnCl_6$: monoclinic. — $B'_2H_2CuCl_4$. — B'HBr: trimetric, $a:b:c = \cdot723:1:\cdot818$. — $B'HCdBr_3$: trimetric. — B'HI.—$B'HBiI_4$ (Kraut, *A.* 210, 323).—B'HF: pearly scales, sol. water and boiling alcohol.— $B'HClO_3$: long white prisms, sol. alcohol and ether, m. sol. water; explodes at 75°.—$B'HClO_4$. —$B'HIO_3$. S.G. $\frac{13}{}$ 1·48. Explodes at 125°-130°. —$B'HCNHg(CN)_2$. [88°]. White needles or tables (Claus a. Merck, *B.* 16, 2737). — $B'_4H_4FeCy_6$: small micaceous crystals, v. sol. water, insol. alcohol and ether (Eisenberg, *A.* 205, 267). — $B'_3H_4FeCy_6$. — $B'_3H_3CoCy_6$. — $B'_2H_2PtCy_4$: triclinic (Scholtz, *M.* 1, 904). — $B'_2H_3PO_4$: laminæ, v. sol. water, ether, and hot alcohol (Nicholson, *A.* 59, 213; Lewy, *B.* 19, 1717). — $B'_2H_3PO_4$. — $B'HPO_3$. — $B'_2H_4P_2O_7$. — $B'_2H_2SO_4$: m. sol. water, sl. sol. alcohol, insol. ether. Does not form an alum with aluminium sulphate (W... *C. N.* 38, 1).—$B'H_2SO_4$: large plates; converted by water into the neutral sulphate (Wellington a. Tollens, *B.* 18, 3313). — $B'_2H_2S_2O_6$ (Malezewsky, *J. R.* 11, 364). — $B'_6(H_2SO_4)_3HI_5$ (Jörgensen, *J. pr.* [2] 14, 384).— $B'HNO_3$. — *Chloro-acetate.* [88°]. — *Di-chloro-acetate.* [122°]. — *Tri-chloro-acetate.* [145°]. — *Oxalate* $B'_2H_2C_2O_4$: triclinic columns, v. sol. water, sl. sol. alcohol, insol. ether. — *Phenate*, B'HOPh. [30°]. (181°) (D.). (185°) (D. a. S.). Crystals resembling naphthalene (from alcohol or light petroleum) (Dyson, *C. J.* 43, 466). Formed by boiling equivalent quantities of phenol and aniline

together Dale a. Schorlemmer, *C. J.* 43, 186). —*Phthalate*, [146°]: needles.—(*β*)-*Naphtholate*, [82·4°]: crystalline powder (from light petroleum) (Dyson, *C. J.* 43, 469). Other salts of aniline are described under the various acids.

Combinations.—(Schiff, *C. R.* 56, 268, 1095; Vohl, *Ar. Ph.* [2] 148, 201; Leeds, *J.* 1882, 500). —$B'_2(SiF_4)_2$: minute needles, insol. benzene or petroleum-spirit; may be sublimed; converted by water or alcohol into aniline silicofluoride (Jackson a. Comey, *B.* 18, 3195). — $B'_4Ag_2SO_4$ 2aq: hair-like crystals (Mixter, *Am.* 1, 239). — B'_2ZnSO_4. — B'_2ZnCl_2. — B'_2ZnBr_2.— B'_2ZnI_2.—$C_6H_5NH.HgCl$: amorphous pp. got by mixing hot alcoholic solutions of aniline and $HgCl_2$ (Forster, *A.* 175, 30).—B'_2HgCl_2: needles, got by mixing cold alcoholic solutions of aniline and $HgCl_2$.—B'_2HgBr_2 [112°] (Klein, *B.* 13, 835). — B'_2HgI_2. [60°]. Decomposed by alcohol.— $B'_2Hg(NO_3)_2$: pp., converted by hot water into $C_6H_5NH.HgNO_3$ ½aq and $(PhN)_2Hg_3(NO_3)_2$ 2aq. —B'_2CaCl_2.—B'_2CdCl_2.—B'_2CdBr_2.—B'_2CdI_2.— $B'_2Cd(NO_3)_2$.—B'_6TiCl_4.—B'_2SnI_2.—B'_3SbCl_3.— $B'_2UrO_2Cl_2$.—B'_2MnCl_2.—B'_2MnBr_2.—B'_2MnI_2.— B'_2FeCl_2.—B'_2SnCl_4.—B'_3AsCl_3. [c. 90°]. (c. 208°). — B'_3SbCl_3. [80°].—B'_3BiCl_3. — $B'BiOCl$. — B'_2CoCl_2 2EtOH: red leaflets, prepared by adding aniline (2 mols.) to an alcoholic solution of $CoCl_2$ (1 mol.); at 100° it becomes blue B'_2CoCl_2 (Lippmann a. Vortmann, *B.* 12, 79). — B'_2NiCl_2 2EtOH: small green needles, similarly prepared; at 100° it becomes yellowish green B'_2NiCl_2 (L. a. V.).—B'_2CuCl_2 (Destrem, *Bl.* 30, 482).—B'_2CuSO_4.—B'_2PtCl_2 (Gordon, *B.* 3, 176; Cochin, *Bl.* 31, 499). — $B'PtCl_2C_2H_4HCl$. — $B'PtCl_2C_2H_4$ (Griess a. Martius, *A.* 120, 326).

Acetyl derivative C_8H_9NO *i.e.* $C_6H_5NH.C_2H_3O$. *Acetanilide.* Mol. w. 135. [114°]. (295°). S. ·34 at 14°; 6·59 at 102·5° (Friswell, *private com.*). V.D. 4·8 (calc. 4·7).

Formation. — 1. From aniline and AcCl (Gerhardt, *A.* 87, 164).—2. By boiling aniline with glacial acetic acid (Greville Williams, *C. J.* 17, 106; *v.* also CHEMICAL CHANGE).—3. By heating aniline with acetamide (Kelbe, *B.* 16, 1199).—4. From acetophenone-oxim and H_2SO_4 at 100° (Beckmann, *B.* 20, 1507).

Properties. — Laminæ (from water); v. sol. alcohol, ether, and benzene. A saturated aqueous solution boils at 102·5° (Friswell).

Reactions. — 1. Passed through a *red-hot tube* it forms di-phenyl-urea, aniline, benzene, and CNH (Nietzki, *B.* 10, 476).—2. $ZnCl_2$ at 260° gives flavaniline $C_{16}H_{14}N_2$. — 3. PCl_5 forms $CH_3.CCl_2NHPh$ which readily splits up into HCl and $CH_3.CCl{:}NPh$. The latter is converted by water into HCl and acetanilide, and by aniline into di-phenyl-acetamidine, $CH_3.C(NHPh){:}NPh$. $CH_3.CCl{:}NPh$ changes a little above its melting point [50°] into the hydrochloride of $CH_3.C(NPh).CH_2.CCl{:}NPh$, [117°] which at 160° changes to the hydrochloride of amorphous $C_{16}H_{14}N_2$ (Wallach, *A.* 184, 86; *cf.* Michael, *J. pr.* [2] 35, 207).—4. P_2S_5 forms thio-acetanilide (Hofmann a. Simpson, *B.* 11, 339; Jacobsen, *B.* 19, 1071; *v.* THIOACETIC ACID).—5. Heating with *sulphur* produces oxalyl-amido-phenyl mercaptan, $C_6H_4{<}^{N}_{S}{>}C.C{<}^{N}_{S}{>}C_6H_4$, and some ethenyl-amido-phenyl mercaptan (Hofmann, *B.* 13, 1226). — 6. *Dry NaOEt* at 170° gives ethyl-aniline AcNHPh + NaOEt = EtNHPh + NaOAc. 7. *Nitrous acid* passed into a solution of acetanilide in glacial HOAc forms an unstable nitrosamine, PhNAc.NO, [41°] (O. Fischer, *B.* 9, 463). — 8. *Nitric acid* converts acetanilide dissolved in 4 pts. of H_2SO_4 chiefly into *p*-nitro-acetanilide, some *o*- being formed. If the acetanilide is dissolved in 20 pts. H_2SO_4 a small quantity of the *m*-compound appears (Nölting a. Collin, *B.* 17, 261).

Sodium acetanilide C_6H_5NAcNa (Runge, *Z.* [2] 6, 119). Formed by distilling off the alcohol from an alcoholic solution of equivalent quantities of acetanilide and sodium ethylate (Seifert, *B.* 18, 1358). Crystalline powder. Absorbs CO_2 in the cold, becoming sodium acetyl-phenyl-carbamate, $C_6H_5NAc.CO_2Na$.

Mercury acetanilide $(C_6H_5NAc)_2Hg$. [215°]. Formed by melting acetanilide with HgO (Oppenheim a. Pfaff, *B.* 7, 624).

Hydrochloride $(C_6H_5.NHAc)_2HCl$ crystallises in needles, decomposed by water. By heating for half-an-hour at 250° it splits off acetic acid and yields the hydrochloride of di-phenyl-acet-amidine $CH_3.C(NPh).NHPh$. By 6 hours' heating at 280° it gives flavaniline. At a still higher temperature quinoline bases are formed in small quantity (Nölting a. Weingärtner, *B.* 18, 1340).

v-Chloro-acetanilide $C_6H_5.NClAc$. *Acetyl-phenyl-chloro-amide.* [172°]. Prepared by adding a conc. solution of bleaching powder to a conc. aqueous solution of acetanilide containing excess of acetic acid, as long as a pp. is formed. Colourless needles. Scarcely soluble in water. Crystallises well from very dilute acetic acid. Heated to 172° it suddenly changes, with explosive violence, to the isomeric *p*-chloro-acetanilide. This change is also produced by cold conc. HCl with a violent reaction. It dissolves in warm absolute alcohol at first unaltered, but after a few moments a violent reaction sets in and the above change takes place. Alkalis and amine bases replace the Cl by H. It converts aceto-acetic ether into chloro-aceto-acetic ether. Not attacked by boiling water (Bender, *B.* 19, 2272).

Diacetyl derivative $C_{10}H_{11}NO_2$ *i.e.* $C_6H_5NAc_2$. [111°]. *Diacetanilide.* From phenyl thiocarbimide and HOAc at 140° (Hofmann, *B.* 3, 770): $PhNCS + 2HOAc = PhNAc_2 + CO_2 + H_2S$. Plates. On distillation it gives acetanilide (Gumpert, *J. pr.* [2] 32, 293).

Benzoyl derivative C_6H_5NHBz. [159°].

Formation.—1. From aniline and BzCl (Gerhardt, *A. Ch.* [3] 37, 327).—2. By the action of phenyl cyanate upon benzene in presence of $AlCl_3$; the reaction probably being:

(*a*) $PhN.CO + HCl = PhNH.COCl$.

(*b*) $PhNH.COCl + C_6H_6 = PhNH.COC_6H_5 + HCl$

(Leuckart, *B.* 18, 873). 3. From benzophenone oxim and H_2SO_4 at 100° (Beckmann, *B.* 20, 1507)

Properties.—Volatile plates; insol. water.

Reactions.—1. PCl_5 forms $PhNH.CCl_2Ph$ and then $PhN{:}CClPh$, [40°] (Wallach, *A.* 184, 79).—2. Boiling with *sulphur* produces benzenyl-amido-phenyl mercaptan.

Oxim $C_{13}H_{12}N_2O$ *i.e.* $C_6H_5.C(NOH)NHC_6H_5$ *Benz-anilidoxim.* [136°] Obtained by heating

thiobenzanilide with hydroxylamine hydrochloride and Na_2CO_3 in alcoholic solution for about an hour (Müller, *B.* 19, 1669). Slender needles. Sol. hot water, alcohol, ether, chloroform, and benzene, sl. sol. ligroïn. Dissolves both in acids and alkalis. Salts.—B'HCl: sol. alcohol.—$B'_2H_2Cl_2PtCl_4$*. *Ethyl ether* $C_6H_5.C(NHPh):NOEt$. [56°]; white pp. *Benzoyl derivative* $C_6H_5.C(NHPh)NOBz$. [116°]; white glistening needles; sol. alcohol, ether, and benzene, insol. water and ligroïn.

Di-benzoyl derivative $NPhBz_2$. [136°]. From benzanilide and BzCl (Gerhardt a. Chiozza, *C. R.* 37, 90).

Preparation.—Benzanilide (18 g.) is heated with BzCl (14 g.) for 3 hours.

Properties.—Needles (from alcohol). With dilute HCl at 120° it gives aniline and benzoic acid (Higgin, *C. J.* 41, 132).

Di-benzoyl derivative $C_6H_4NBz_2$. [160°] (isomeric with preceding?). From benzoic acid (13 g. and phenyl thiocarbimide (6 g.) at 220° for 6 hours (Losanitch, *B.* 6, 176; Higgin, *C. J.* 41, 133): $PhN:CS + 2HOBz = PhNBz_2 + CO_2 + H_2S$.

Properties.—Plates (from alcohol). With dilute HCl at 120° it gives aniline and benzoic acid.

ANILINE BLACK $C_{30}H_{25}N_5$. *Nigraniline.* Formed by mixing aniline, a chlorate (of K, Na, or Ba) and a metallic salt (of Cu, Fe, V, Mn, or Ce) (Lightfoot, *C. N.* 11, 65; Lauth, *Bl.* [2] 2, 416; Higgin, *Bl.* [2] 7, 93; Guyard, *Bl.* [2] 25, 58; Rosenstiehl, *Bl.* [2] 25, 356; *C. R.* 81, 1257; Kruis, *D. P. J.* 222, 347; Goppelsröder, *C. R.* 82, 331, 1392; Coquillion, *C. R.* 81, 408; Glenk, *D. P. J.* 248, 234). The quantity of metallic salt may be small; ammonium vanadate added to a solution of aniline hydrochloride (6 pts.) and $NaClO_3$ or $KClO_3$ (4 pts.) in water (100 pts.) converts 100,000 times its weight of aniline into black. An aniline black is formed at the positive pole when a solution of an aniline salt is electrolysed. Aniline black is purified by washing with water, alcohol, ether, and benzene. It is the hydrochloride of a base, $C_{30}H_{25}N_5 2HCl$; and can be reduced by tin and HCl, or by HI and P, to *p*-phenylene-diamine and *p*-diamido-diphenylamine $NH_2.C_6H_4.NH.C_6H_4.NH_2$ (Nietzki, *B.* 11, 1093). Electrolytic aniline black appears to be $C_{24}H_{20}N_4 2HCl$ (Goppelsröder).

ANILINE CARBOXYLIC ACID *v.* PHENYL-CARBAMIC ACID.

ANILINE DYES *v.* ROSANILINE, MAUVEÏNE, CHRYSANILINE &c.

ANILOTIC ACID is Nitro-salicylic acid *v.* NITRO-OXY-BENZOIC ACID.

ANILOXALBENZAMIC ACID *v.* PHENYL-OXAMIDO-BENZOIC ACID.

ANIL-PYRUVIC ACID $C_9H_9NO_2$ *i.e.* $CH_3.C(NPh).CO_2H$. [122°]. Formed by the action of aniline on pyruvic acid (Böttinger, *B.* 16, 1924; *A.* 188, 336). Crystals, v. sol. water. In contact with water it condenses to aniluvitonic or (*Py.* 3, 1)-methyl-quinoline carboxylic acid (*q.v.*). On bromination it yields tribromanil-dibromopyruvic acid. Salt.—BaA'_2: v. e. sol. water.

ANIL-UVITONIC ACID *v.* (*Py.* 3)-METHYL QUINOLINE (*Py.* 1)-carboxylic acid.

ANISAMIDE. Amide of methyl-*p*-OXY-BENZOIC ACID.

ANISANILIDE. Anilide of methyl-*p*-OXY-BENZOIC ACID.

ANIS-BENZ-ANIS-HYDROXYLAMINE *v.* HYDROXYLAMINE.

ANIS-BENZ-HYDROXAMIC ACID *v.* HYDROXYLAMINE.

DI-ANIS-BENZ-HYDROXYLAMINE *v.* HYDROXYLAMINE.

ANISE, OIL OF. The essential oil obtained by distilling the seeds of *Pimpinella anisum* or *Illicium anisatum* with water. It contains anethol (*q.v.*). If the oil is heated with dilute HNO_3 (S.G. 1·2) and the resulting heavy oil shaken with warm $NaHSO_3Aq$, so-called anisoïc or thianisoïc acid $C_{10}H_{14}SO_4$ [below 100°] is formed (Limpricht a. Ritter, *A.* 97, 364; Staedeler a. Wächter, *A.* 116, 169). It is a very soluble crystalline mass. $NH_4A'aq.$—$NaA'aq.$—$MgA'_2 5aq.$—$CaA'_2 2aq.$—$BaA'_2 3aq.$—AgA'.

ANISE CAMPHOR. A name for anethol (*q.v.*).

ANISHYDRAMIDE $C_{24}H_{24}N_2O_3$ *i.e.* $(MeO.C_6H_4.CH)_3N_2$. *Tri-methyl-tri-oxy-hydrobenzamide.* [c. 120°]. Formed by action of conc. NH_3Aq upon *p*-methoxy-benzoic (anisic) aldehyde. Prisms, insol. water, sol. boiling alcohol, ether, or conc. HClAq (Cahours, *A. Ch.* [3] 14, 487; Bertagnini, *A.* 88, 128). Changes at 170° into Anisin, a basic isomeride which forms salts: B'HCl aq.—$B'_2H_2PtCl_6$.

ANIS-HYDROXAMIC ACID *v.* HYDROXYLAMINE.

ANISIC ACID *v. p-Methyl*-OXY-BENZOIC ACID.

ANISIC ALDEHYDE *v. p-Methyl*-OXY-BENZOIC ALDEHYDE.

ANISIC ALCOHOL *v. p-Methyl*-OXY-BENZYL ALCOHOL.

ANISIDINE *v.* Methyl derivative of AMIDO-PHENOL.

ANISIL $C_{16}H_{14}O_4$ *i.e.* $C_6H_4(OMe)—CO—CO—C_6H_4(OMe)$. [133°]. Prepared by oxidation of anisoïn with Fehling's solution (Bösler, *B.* 14, 327). Yellow needles. Distils undecomposed. Sol. hot, sl. sol. cold, alcohol, insol. water. On boiling with alcoholic KOH it gives anisilic acid.

ANISILIC ACID $C_{16}H_{16}O_5$ *i.e.* $(MeO.C_6H_4)_2C(OH).CO_2H$. [164°]. Prepared by boiling anisil with alcoholic KOH (Bösler, *B.* 14, 328). Slender white needles. Sol. alcohol, sl. sol. water. Dissolves in strong H_2SO_4 with a violet colour. On oxidation with CrO_3 it gives di-methoxy-benzophenone.

ANISIN *v.* ANISHYDRAMIDE.

ANISOÏN $C_{16}H_{16}O_4$ *i.e.* $MeO.C_6H_4CH(OH).CO.C_6H_4.OMe$. *Di-methyl-tri-oxy-phenyl-benzyl-ketone.* [113°]. Prepared by boiling *p*-methoxy-benzoic (anisic) aldehyde with alcoholic KOH (yield 60 p.c.; Bösler, *B.* 14, 326), or KCy (Rossel, *Z.* [2] 5, 562). Needles; v. sl. sol. water, sl. sol. cold alcohol and ether. Strong H_2SO_4 dissolves it with red colour, rapidly changing to pale green, and on heating, to yellow and then purple. See also HYDRO-ANISOÏN.

ANISOÏC ACID *v.* ANETHOL.

ANISOL *v. Methyl*-PHENOL.

ANISOL-ISATIN *v. Di-methyl-di*-OXY-DI-PHENYL-OXINDOLE.

ANISOL-PHTHALIC ACID *v. Methyl*-OXY-BENZOPHENONE CARBOXYLIC ACID.

ANISONITRILE *v.* *Nitrile of Methyl-p*-OXY-BENZOIC ACID.

ANISO-DIUREÏDE *v.* *Methyl*-OXY-BENZENYL-DI-UREA.

ANISURIC ACID $C_{10}H_{11}NO_4$ *i.e.* $MeO.C_6H_4.CO.NH.CH_2.CO_2H$. *Methyl-oxy-benzoyl-glycocoll.*—From silver amido-acetate and methyl-*p*-oxy-benzoyl chloride. Also secreted when methyl-*p*-oxy-benzoic (anisic) acid is taken into the stomach. Laminæ. Split up by acids into glycocoll and anisic acid.

Salts: CaA'_2 3aq.—AgA' (Cahours, *A.* 103, 90; 109, 32; Graebe a. Schultzen, *A.* 142, 348).

ANISYL. This name is usually given to the radicle methyl-*p*-oxy-phenyl, $CH_3O.C_6H_4$, but sometimes also to methyl-*p*-oxy-benzoyl, $CH_3O.C_6H_4.CO$, which could more appropriately be called anisoyl.

ANISYL BROMIDE *v.* *p*-BROMO-PHENOL, *Methyl-ether* and *Methyl*-OXY-BENZOYL BROMIDE.

ANISYL CARBAMIDE *v.* *Methyl-p*-OXY-PHENYL-UREA.

ANISYL CHLORIDE *v.* *p*-CHLORO-PHENOL, *Methyl-ether* and *Methyl*-OXY-BENZOYL CHLORIDE.

ANISYL METHYL KETONE *v.* *Methyl*-OXY-ACETOPHENONE.

ANISYL-THIO-UREA *v.* *Methyl*-OXY-PHENYL-THIO-UREA.

ANISYL-UREA *v.* *Methyl*-OXY-PHENYL-UREA.

ANOL $C_9H_{10}O$ *i.e.* $HO.C_6H_4.CH:CH.CH_3$. [92·5°]. (c. 250°). Formed by heating anethol with KOH. Shining laminæ (from alcohol, ether, and chloroform) sol. KOHAq and reppd. by acids (Ladenburg, *B.* 2, 371).

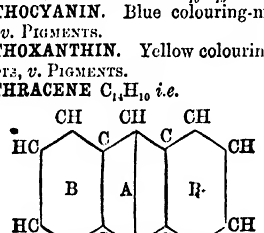
ANTHEMENE $C_{18}H_{36}$. [64°]. (440°). S.G. ^{15} ·942. V.D. 127 (calc. 131). S. (alcohol) ·033 at 25°. Extracted from flowers of chamomile (*Anthemis nobilis*) by light petroleum (Naudin, *Bl.* [2] 41, 483). Minute needles, insol. water, sol. ether, petroleum, CS_2, chloroform, and hot alcohol.

ANTHEMOL $C_{10}H_{16}O$. (214°). Occurs in oil of chamomile (*Anthemis nobilis*). Thick liquid with camphor-like smell (Koebig, *A.* 195, 104). Boiling dilute HNO_3 produces terephthalic and *p*-toluic acids. *Acetyl derivative* $C_{10}H_{15}OAc$. (235°).

ANTHOCYANIN. Blue colouring-matter of flowers *v.* PIGMENTS.

ANTHOXANTHIN. Yellow colouring matter of flowers, *v.* PIGMENTS.

ANTHRACENE $C_{14}H_{10}$ *i.e.*



Mol. w. 178. [213°]. (c. 360°). H.F.p. –115,000 (v. Rechenberg). S.V. 195·8 (Ramsay). Alcoholic solutions containing less than ·03 p.c. exhibit absorption bands in the ultra-violet part of the spectrum (Hartley, *C. J.* 39, 162). S. (ether) 1·17 at 15°; S. (HOAc) ·44 at 15°. S. (benzene) 1·7 at 15°. S. (alcohol) ·08 at 16°; (dilute alcohol, S.G. ·84) ·46 at 15° (Versmann, *J.* 1874, 423; Becchi, *B.* 12, 1978).

Occurrence.—In coal tar (Dumas a. Laurent, *A. Ch.* [2] 50, 187). From crude anthracene the following bodies may be extracted by acetic ether:—(*a*) Soluble in cold alcohol: carbazol, phenanthrene, fluorene, and a hydrocarbon [130°]. Carbazol is insoluble in CS_2, the others dissolve, but can be separated by their picrates. (*b*) Soluble in cold benzene: synanthrene and two hydrocarbons [104°] and [97°].—(*c*) Soluble in hot benzene: anthracene (insoluble in dilute alcohol) and pseudophenanthrene (soluble in dilute alcohol).—(*d*) Insoluble in benzene: carbazol (Zeidler, *A.* 191, 302).

Formation.—1. By passing through red-hot tubes a mixture of ethylene with benzene, diphenyl, or chrysene; or a mixture of benzene and styrene (Berthelot, *Bl.* [2] 7, 223; 8, 231; 9, 295) or benzene and petroleum (Letny, *B.* 10, 412; 11, 1210), or benzene and oil of turpentine (Schultz, *B.* 7, 113).—2. By passing benzyl-toluene, $Ph.CH_2.C_6H_4.CH_3$, through a red-hot tube, or over heated litharge (Behr a. Dorp, *B.* 6, 754; *A.* 169, 216).—3. By action of $AlCl_3$ on a mixture of benzene and *s*-tetra-bromo-ethane (Anschütz a. Eltzbacher, *B.* 16, 623).—4. By action of sodium on *o*-bromo-benzyl bromide (Jackson a. White, *Am.* 2, 392; *B.* 12, 1965).—5. By heating benzyl ethyl oxide, $PhCH_2.O.Et$, with P_2O_5 (J. Schulze, *J. pr.* [2] 27, 518).—6. By action of $CHCl_3$ or CH_2Cl_2 on benzene in presence of $AlCl_3$ (Friedel, Crafts, a. Vincent, *Bl.* [2] 40, 97; 41, 325).—7. By heating benzyl chloride with water at 200° and distilling the product (Limpricht, *A.* 139, 303; Zincke, *B.* 7, 278).—8. By heating a mixture of alizarin with zinc dust at low red heat (Graebe a. Liebermann, *A. Suppl.* 7, 297).—9. By distilling *o*-tolyl phenyl ketone with zinc dust (Behr a. Dorp, *B.* 7, 17).—10. Together with toluene by the action of $AlCl_3$ on benzyl chloride (Perkin a. Hodgkinson, *C. J.* 37, 726).—11. By distilling benzyl-phenol with P_2O_5 (Paterno a. Fileti, *B.* 6, 1202).—12. By heating *o*-benzoyl-benzoic acid with zinc dust (Gresly, *A.* 234, 238).

Properties.—Four- or six-sided monoclinic white tables with blue fluorescence. Insol. water, sl. sol. alcohol, ether, benzene, glacial HOAc, chloroform, CS_2, and light petroleum. Changed in sunlight into para-anthracene (paraphotene) [244°], which is insoluble in most menstrua, but is reconverted into anthracene by fusion.

Estimation.—Anthracene (1 g.) is dissolved in boiling glacial HOAc (45 c.c.), filtered if necessary, and a solution of CrO_3 (10 g.) in glacial HOAc (5 c.c.) diluted with water (5 c.c.) is slowly added; a slight excess of CrO_3 should be left after long boiling. The liquid is diluted with water (150 c.c.) and the ppd. anthraquinone washed, dried at 100°, and weighed (Luck, *B.* 6, 1347; *v.* also Meister, Lucius, a. Brüning, *Fr.* 16, 61; Paul a. Cownley, *C. N.* 28, 175; Lucas, *C. N.* 30, 190; Nicol, *C. J.* 30, 553; J. T. Brown, *C. J.* 31, 232; Versmann, *C. J.* 30, 347).

Reactions.—1. Conc. HI at 280° forms anthracene hydrides, toluene, and various paraffins. 2. *Chromic acid* produces anthraquinone.—3. *Nitric acid* also produces anthraquinone, and not nitro-anthracene.—4. *Sulphuric acid* forms sulphonates.—5. $COCl_2$ forms the chloride of anthracene (*A*)-carboxylic acid.—6. H_2O_2 produces anthraquinone (Leeds, *B.* 14, 1382).

Combinations.—With picric acid it forms

$C_{14}H_{10}C_6H_2(NO_2)_3OH$ [188°]; red needles.—With dinitrothiophene: $C_{14}H_{10}C_4H_2(NO_2)_2S$ [162°] (Rosenberg, *B.* 18, 1778).—With nitric acid: $C_{14}H_{10}NO_3H$ [125°]. Formed by passing nitrous fumes into anthracene suspended in glacial HOAc at 20°. White needles or prisms, sol. alcohol or benzene, unstable when damp; converted by alkalis into nitroso-anthrone $C_{14}H_9NO_2$, [146°] and nitroso-hydroanthrone $C_{14}H_{11}NO_2$ (Liebermann a. Lindermann, *B.* 13, 1535).—With nitric peroxide: $C_{14}H_{10}N_2O_4$ [194°]. Formed by passing nitrous fumes into anthracene dissolved in glacial acetic acid cooled below 15°. Needles or plates, sl. sol. alcohol and benzene; unstable when damp; converted by alkalis into nitroso-anthrone.—Hydro-anthracene-nitrite, $C_6H_4{:}C_2H_2(ONO)_2{:}C_6H_4$ (?) [125°] is isomeric with the last body. It is formed by the action of HNO_3 on an acetic acid solution of anthracene-di-hydride. Small crystals. Easily soluble in benzene. On boiling with alkalis nitroso-oxanthranol dissolves whilst nitronitrosoanthrone remains insoluble. Oxidation with CrO_3 converts it into anthraquinone (Liebermann a. Landshoff, *B.* 14, 467).

Constitution.—The constitutional formula given above is founded chiefly upon *Formation* 3, 4, and 2, and upon the formula assigned to anthraquinone (*q. v.*). Substitution in one of the benzene nuclei may be indicated by *B* prefixed to a number exactly as in the naphthalene-derivatives; substitution in the C_2H_2 group is indicated by the prefix *A*. But in this dictionary the notation employed for anthracene derivatives is usually exactly the same as that used for other benzene compounds (*v.* BENZENE).

Additional References.—Graebe a. Liebermann, *Z.* [2] 4, 279, 503, 724; 5, 602; 6, 257; Fritzsche, *N. Petersb. Acad. Bull.* 9, 385; 13, 531. *V.* also METHYL-ANTHRACENE, ETHYL-ANTHRACENE, BUTYL-ANTHRACENE, AMYL-ANTHRACENE, and their hydrides; also CHLORO-, BROMO-, NITRO-, ANTHRACENE, ANTHRAMINE, ANTHROL, ANTHRANOL and SULPHO-ANTHRACENE CARBOXYLIC ACID.

Isoanthracene $C_{14}H_{10}$. [134°]. Obtained by passing di-benzyl-toluene, $C_{21}H_{20}$ (from toluene, benzyl chloride, and zinc dust) through a red-hot tube (Weber a. Zincke, *B.* 7, 1156). Laminæ; more soluble than anthracene. Converted by CrO_3 into a quinone $C_{14}H_8O_2$.

Para-anthracene $C_{14}H_{10}$. [244°]. Deposited when solutions of anthracene are exposed to sunlight. V. sl. sol. alcohol, ether, and benzene. Changed into anthracene by fusion. Does not combine with picric acid (Schmidt, *J. pr.* [2] 9, 248).

ANTHRACENE BROMIDE $C_{14}H_{10}Br_2$. Crystals formed by adding bromine to a solution of anthracene in CS_2 at 0° (Perkin, *C. N.* 39, 145). Split up by heat into HBr and bromo-anthracene.

ANTHRACENE CARBOXYLIC ACID $C_{15}H_{10}O_2$ *i.e.* $C_{14}H_9.CO_2H$. [280° corr.]. Two anthracene carboxylic acids can be obtained by distilling dry crude potassium anthracene sulphonate with K_4FeCy_6, and saponifying the mixture of nitriles that results (Liebermann, *B.* 8, 246; 13, 48). They may be separated by baryta-water which forms a soluble salt with the (β)-acid, and an insoluble one with the (γ)-acid. Nevertheless the two acids may be identical.

(β)-**Anthracene carboxylic acid.** [c. 260°]. Yellow needles (from alcohol). Insol. water, sl. sol. benzene and ether. Gives anthracene when heated with soda-lime, and anthraquinone carboxylic acid when oxidised by CrO_3. Salts with heavy metals are v. sol. water. The acid and its salts show blue fluorescence.

(γ)-**Anthracene carboxylic acid.** [c. 280°]. Formed also by reducing anthraquinone carboxylic acid with zinc dust and ammonia (Börnstein, *B.* 16, 2609). Small plates or needles. May be sublimed. Sol. acetic acid and hot alcohol, sl. sol. cold alcohol and chloroform. Its solutions have a blue fluorescence. CrO_3 gives anthraquinone carboxylic acid [285°].

Salts.—NaA′: small spangles, sl. sol. water; fluorescent. All the salts of the heavy metals are tolerably insoluble.

Ethyl ether A′Et: [135°], white plates, with blue fluorescence.

Chloride $C_{14}H_9.COCl$: yellow crystals, soluble in alcohol, ether, benzene, and CS_2 with an intense green fluorescence.

Amide $C_{14}H_9.CONH_2$: [295°], slender yellow needles or plates, sl. sol. alcohol with a blue fluorescence, insol. water, benzene, CS_2 and chloroform.

Anthracene (*A.*)-carboxylic acid $C_6H_4{:}C_2H(CO_2H){:}C_6H_4$. [206°]. From anthracene and $COCl_2$ at 200°, and saponifying the chloride by Na_2CO_3Aq (Graebe a. Liebermann, *B.* 2, 678). Formed also by heating (*A.* 1)-chloro-anthracene (*A.* 2)-carboxylic acid with alcoholic potash (Behla, *B.* 20, 701). Silky needles (from alcohol); decomposed by heat into CO_2 and anthracene. V. sl. sol. water. CrO_3 gives anthraquinone. Cl or Br (1 mol.) gives (*A.* 1)-chloro- (or bromo-) anthracene (*A.* 2)-carboxylic acid. A larger quantity (2 mols.) of Cl or Br give (*A.*)-di-chloro- (or bromo-) anthracene. Conc. H_2SO_4 gives (*B.*)-sulpho-anthracene (*A.*)-carboxylic acid. Salt.—AgA′.

Methyl ether MeA′. [111°]. Yellowish prisms or tables.

Anthracene-di-*m*-carboxylic acid

$$C_6H_4\Big\langle\begin{matrix}\overset{(1)}{CH}\\ |\\ \underset{(6)}{CH}\end{matrix}\Big\rangle C_6H_2(CO_2H)_2^{(2:4)}$$

[above 330°]. Formed by reduction of an ammoniacal solution of the corresponding anthraquinone-*m*-di carboxylic acid with zinc-dust. Crystalline powder. Scarcely sol. water, m. sol. other solvents (Elbs a. Günther, *B.* 20, 1365).

Anthracene-di-carboxylic acid

$$C_6H_4\Big\langle\begin{matrix}\overset{(1)}{CH}\\ |\\ \underset{(6)}{CH}\end{matrix}\Big\rangle C_6H_2(CO_2H)_2^{(3:4)}$$

[345°]. Formed by reduction of an ammoniacal solution of anthraquinone-di-carboxylic acid [340°] with zinc-dust. Yellow crystalline powder. Scarcely sol. water, sl. sol. other solvents (Elbs a. Eurich, *B.* 20, 1363).

ANTHRACENE CHLORIDE $C_{14}H_{10}Cl_2$. From anthracene dissolved in CS_2 at 0° by passing in Cl (Perkin, *C. J.* 31, 209). Needles (from

benzene). Splits up into HCl and chloranthracene even in the cold.

ANTHRACENE HYDRIDES.

Anthracene di-hydride $C_{14}H_{12}$. [108°]. (313°). Formed by heating anthracene at 160° with HI and red P, or by treating a solution in alcohol (95 p.c.) with sodium-amalgam. Prepared by heating anthraquinone (30 pts.), HI (140 pts. of S.G. 1·8), and red P (10 pts.) with inverted condenser for one hour on a sand bath (Liebermann, *A. Suppl.* 7, 265; 212, 5). Large monoclinic plates (from alcohol) or needles (by sublimation). Insol. water, v. sol. alcohol, ether, and benzene. Volatile with steam. Its solutions fluoresce blue.

Reactions.—1. Warm conc. H_2SO_4 forms anthracene and SO_2.—2. Br added to its solution in CS_2 forms di-bromo-anthracene.—3. Conc. *nitric acid* forms hydro-anthracene-nitrite (*v. sup.*) and dinitroanthrone.—4. CrO_3 gives anthraquinone.

Anthracene hexa-hydride $C_{14}H_{16}$. [63°]. (290°). From oxy-anthraquinone (or anthracene dihydride), fuming HI and red P by boiling for 20 hours (Liebermann, *A.* 212, 25; *Suppl.* 7, 273). Plates (from alcohol). Volatile with steam; v. sol. alcohol, ether, and benzene. At a red heat it is split up into hydrogen and anthracene.

ANTHRACENE - HYDRIDE CARBOXYLIC ACIDS.

Anthracene-di-hydride carboxylic acid $C_{15}H_{12}O_2$ *i.e.* $C_{14}H_{11}(CO_2H)$. [203°]. Formed, together with the following acid, by reduction of anthracene-carboxylic acid, [280° cor.], with sodium-amalgam (Börnstein, *B.* 16, 2612). Colourless plates. V. sol. ordinary solvents.

Anthracene-tetra-hydride carboxylic acid $C_{14}H_{13}(CO_2H)$. [165°]. Colourless trimetric tables.

Anthracene-hexa-hydride carboxylic acid $C_{14}H_{15}(CO_2H)$. [232°]. Formed by reduction of anthracene-carboxylic acid by heating it with HI (1·7) and P at 220° (B.). Slender needles.

ANTHRACENE-DI-HYDRIDE SULPHONIC ACID $C_{14}H_{11}.HSO_3$. Prepared by reduction of sodium anthraquinone sulphonate with HI (S.G. 1·8) and red P (Liebermann, *B.* 12, 189, *A.* 212, 44). Decomposed by fusion with KOH with formation of anthracene and anthracene hydride. NaA′aq: long soluble needles.—BaA'_2.—CaA'_2.

ANTHRACENE SULPHONIC ACID $C_{14}H_9SO_3H$.

Formation.—From anthraquinone sulphonic acid, HI (S G. 1·7), and red P, by boiling for half an hour (Liebermann, *A.* 212, 48).

Preparation.—From sodium anthraquinone sulphonate (500 g.), zinc dust (750 g.) and ammonia (3 litres of S.G. ·88), at 100° (*A.* 212, 57; *B.* 15, 852). On oxidation by HNO_3 it gives anthraquinone sulphonic acid.

Salts.—NaA′4aq, v. sl. sol. water.—BaA'_2.—PbA'_2 2aq.

The existence of (α)- and (β)-anthracene sulphonic acids amongst the disulphonic acids obtained by sulphonation of anthracene (Linke, *J. pr.* [2] 11, 222) has been denied by Liebermann (*B.* 12, 592).

(α)-Anthracene-disulphonic acid
$\left[1\,{}^2_3\right]$ $C_6H_3(SO_3H):C_2H_2:C_6H_3SO_3H$ $\left[{}^2_3\,4\right]$.

Preparation.—1 pt. of anthracene is gently heated on a water bath with 3 pts. of H_2SO_4 for an hour. *After dilution with water, the filtered solution is neutralised with* $PbCO_3$, and the lead salts converted into the sodium salts.

Since the sodium salt of the (α)-acid is much less soluble in water containing Na_2CO_3 than the sodium salt of the (β)-acid it can be readily separated from the latter (which is formed simultaneously) (Liebermann a. Boeck, *B.* 11, 1613; 12, 182, 1287).

Properties.—Minute needles. By fusion with KOH it gives (α)-dioxyanthracene (chrysazol), which is converted on oxidation into chrysazin *v.* DI-OXY-ANTHRAQUINONE.

Salts.—Na_2A'' 4aq.—K_2A'' aq.—CaA″ 5aq.—BaA″ 4aq.

(β)-Anthracene-disulphonic acid
$\left[1\,{}^2_3\right]$ $C_6H_3(SO_3H):C_2H_2:C_6H_3.SO_3H$ $\left[{}^2_3\,1\right]$.

Preparation.—1 pt. of anthracene is heated to 100°C. with 3 pts. of H_2SO_4 till half has dissolved. It is separated from the (α)-acid, simultaneously formed, by conversion into the sodium salt. By fusion with KOH it gives a dioxyanthracene, which on oxidation is converted into anthrarufin *v.* DI-OXY-ANTHRAQUINONE.

Salts.—Na_2A'' 3aq; white leaflets, easily soluble with a blue fluorescence.—BaA″ 4aq; white leaflets.—A″Pb: crystalline pp.—CaA″ 3aq (Liebermann a. Boeck, *B.* 11, 1613; 12, 182, 1287).

Anthracene - di - sulphonic acid (*Flav-*). $C_{14}H_8(SO_3H)_2$. Prepared by reduction of sodium (α)-anthraquinone di-sulphonate with zinc-dust and NH_3 (Schüler, *B.* 15, 1807).

Salts.—$A''Na_2$: soluble crystals, its solutions have a blue-violet fluorescence.—A″Ba: white crystalline powder.

ANTHRACHRYSONE *v.* *tetra*-OXY-ANTHRAQUINONE.

ANTHRACYL-AMINE *v.* ANTHRAMINE.

ANTHRAFLAVIC ACID *v.* DI-OXY-ANTHRAQUINONE.

ANTHRAGALLOL *v.* (1, 2, 3)-*tri*-OXY-ANTHRAQUINONE.

ANTHRAHYDROQUINONE *v.* OXANTHRANOL.

ANTHRAMINE $C_{14}H_{11}N$ *i.e.* $C_6H_4:(C_2H_2):C_6H_3NH_2$. *Anthracylamine. Amido-anthracene. Anthrylamine.* [237°].

Formation. — 1. By heating amido-anthraquinone with HI and P.—2. By heating anthrol with acetamide at 280° and saponifying the acetyl derivative so produced.—3. By heating anthrol with 10 p.c. aqueous NH_3 at 250°; the yield is nearly theoretical.—4. By heating anthrol with alcohol and ammonia at 170°.

Properties.—Yellow plates (from alcohol). May be sublimed; sl. sol. alcohol, the solution having a splendid green fluorescence. Is a weak base, dissolving with difficulty in boiling HCl. Forms a blue mass when fused with arsenic acid. Is readily methylated.

Reactions.—1. Does not give the carbamine or mustard oil tests.—2. Boiling HOAc gives di-anthramine.—3. Chloroform and alcoholic potash give rise to di-anthryl-formamidine $C_{14}H_9.NH.CH:N.C_{14}H_9$.—4. *Nitrous acid* gives $C_{28}H_{21}N_3O$, [250°], a body which forms a red solution in CS_2, and a blue solution in H_2SO_4.

Salts.—B′HCl: white iridescent plates, sl. sol. water; formed by adding HCl to an alcoholic

solution of the base. Its solution does not fluoresce.—$B'_2H_2SO_4$: v. sl. sol. water.

Acetyl derivative $C_{14}H_9NHAc$. [240°]. Plates. Its alcoholic solution fluoresces blue. CrO_3 gives acetyl-amido-anthraquinone.

Formyl derivative $C_{14}H_9NH.CHO$. [242°]. Small yellowish-green crystals, sl. sol. alcohol, with green fluorescence.

References.—Roemer, *B.* 15, 223; Liebermann a. Bollert, *B.* 15, 226, 852; 16, 1635; *A.* 212, 57.

Di-anthramine $C_{28}H_{19}N$ *i.e.* $(C_{14}H_9)_2NH$. *Di-anthracylamine.* Prepared by boiling anthramine with acetic acid (Bollert, *B.* 16, 1636). Does not melt at 320°. Small glistening plates. Very sparingly soluble in all solvents.

ANTHRAMINE-DI-HYDRIDE $C_{14}H_{11}.NH_2$. Slender colourless needles. Very soluble in alcohol. Formed by reduction of anthramine with sodium-amalgam.—B'HCl: sparingly soluble white needles (Liebermann a. Bollert, *B.* 15, 853).

ANTHRANIL C_7H_5NO *i.e.* $C_6H_4<\begin{matrix}CO\\NH\end{matrix}>$ (?).

o-Amido-benzoic lactam. (c. 213°). V.D. 4·14 (obs.). Formed by reduction of *o*-nitro-benzaldehyde with tin and acetic acid (Friedlander a. Henriques, *B.* 15, 2105). Colourless oil; volatile with steam. Soluble in ordinary solvents, but sparingly in water. Very weak basic properties. Reduces salts of gold and silver to the metal. By alkalis it is converted into anthranilic acid of which it is the anhydride. *Double compound* $C_7H_5NOHgCl_2$: [174°]; slender needles, sol. alcohol and hot water, sl. sol. cold water.

Benzoyl derivative $C_6H_4<\begin{matrix}CO\\|\\NBz\end{matrix}$. [123°]. (above 360° with decomposition). Formed by heating isatoïc acid with BzCl (E. v. Meyer, *J. pr.* [2] 33, 19). Long white needles; readily takes up H_2O forming benzoyl-anthranilic acid (Friedlander a. Wleugel, *B.* 16, 2229).

ANTHRANIL *v*-**CARBOXYLIC ACID** *v.* Isatoic acid.

ANTHRANILIC ACID *v. o*-Amido-benzoic acid.

ANTHRANOL $C_{14}H_{10}O$ *i.e.*

$$C_6H_4<\begin{matrix}C(OH)\\|\\CH\end{matrix}>C_6H_4.$$ (163°–170°). From anthraquinone (30 g.), HI (140 g. of S.G. 1·75), and red P (8 g.), by 15 minutes' digestion (Liebermann, *A.* 212, 6). Needles (from benzene). Its alcoholic solution shows blue fluorescence. Decomposed by heat, becoming greenish. Dissolves in aqueous KOH, forming a yellow liquid, whence CO_2 pps. the anthranol. The alkaline solution is oxidised by air, some anthraquinone being formed. CrO_3 in glacial HOAc completely oxidises anthranol to anthraquinone.

Acetyl derivative. [126°–131°]. White needles (from dilute alcohol).

ANTHRANOL DIHYDRIDE

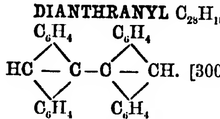
$$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>C_6H_4.\quad [76°].$$

Preparation.—50 grms. of anthraquinone are mixed with 100 grms. of zinc dust and heated over a water-bath with 300 c.c. ammonia and 200 c.c. of water. The liquid turns at first blood-red from oxanthranol, but after three hours this is reduced, the liquid becoming yellow. The liquid is filtered, the pp. dried at 15°, and extracted with boiling benzoline (40°–60°), from which the anthranol dihydride crystallises on cooling (H. R. v. Perger, *J. pr.* [2] 23, 139).

Properties.—Slender satiny needles, which dissolve in benzoline, forming a solution with bluish fluorescence. May be crystallised from boiling water, but by long-continued boiling with water or with alcohol it is converted into anthracene:

$$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>C_6H_4 = C_6H_4<\begin{matrix}CH\\|\\CH\end{matrix}>C_6H_4 + H_2O.$$

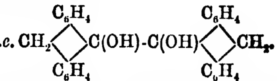
DIANTHRANYL $C_{28}H_{18}$ *i.e.*



[300°]. Yellowish plates. Formed by heating anthrapinacone $C_{28}H_{22}O_2$ with acetyl chloride (K. Schulze, *B.* 18, 3035).

ANTHRAPINACONE

$C_{28}H_{22}O_2$ *i.e.*

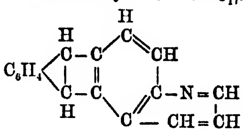


[c. 182°]. Formed as a by-product of the reduction of anthraquinone to dihydroanthranol by means of zinc-dust and NH_3. Long slender white needles. Sol. hot benzene, toluene, or xylene, sl. sol. alcohol, insol. petroleum-ether. On heating with acetyl chloride, $2H_2O$ is removed giving dianthranyl $C_{28}H_{18}$ (Schulze, *B.* 18, 3034).

ANTHRAPURPURIN *v. Tri*-Oxy-anthraquinone.

ANTHRAQUINOL *v.* Oxanthranol.

ANTHRAQUINOLINE $C_{17}H_{11}N$ *i.e.*



[170°]. (446°).

Formation.—1. By heating alizarin-blue with zinc-dust.—2. By heating a mixture of anthramine, nitrobenzene, glycerin, and H_2SO_4 (Graebe, *B.* 17, 170; *A.* 201, 344).

Properties.—Tables, insol. water, sol. alcohol and ether; its solutions show intense blue fluorescence. Its salts are yellow and possess in solution an intense green fluorescence. B'HCl.—$B'_2H_2PtCl_6$.—B'HI.—$B'H_2SO_4$.

Combinations.—With picric acid it forms $C_{17}H_{11}N\ C_6H_2(NO_2)_3OH$: slender yellow needles. With ethyl iodide: B'EtI; golden needles, v. sol. hot, sl. sol. cold, water.

Quinone $C_{17}H_9NO_2$. [185°]. Formed from the preceding by CrO_3. Yellow prisms or needles, insol. water, sol. in alcohol and ether. Salts.—B'HCl: sulphur-yellow needles, sl. sol. water, but slowly decomposed by it.—$B'_2H_2PtCl_6$. Picric acid compound $B'C_6H_3N_3O_7$: golden needles.

ANTHRAQUINONE

$C_{14}H_8O_2$ *i.e.* $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$. Mol. w. 208.

[273°]. S. (alcohol) ·05 at 18°; 2·25 at 78°. V.D. 7·33 (calc. 7·20) (Graebe, *B.* 5, 15).

Formation.—1. By oxidation of anthracene (Laurent, *A. Ch.* [2] 60, 220; 72, 415; *A.* 34, 287; Anderson, *C. J.* 15, 44).—2. From phthalyl chloride by heating with benzene and zinc-dust in sealed tubes at 220° (Piccard, *B.* 7, 1785) or

by treatment with $AlCl_3$ (Friedel a. Crafts, *Bl.* [2] 29, 49).—3. *By dry distillation of calcium* phthalate (Panaotovits, *B.* 17, 312).—4. Together with benzophenone by distillation of calcium benzoate (Kekulé a. Franchimont, *B.* 5, 908).—5. By heating *o*-(but not *p*-) benzoyl-benzoic acid with P_2O_5 at 200° and extracting with benzene (yield 20 p.c.; Behr a. Van Dorp, *B.* 7, 578).—6. In small quantity, by distilling benzoic acid with P_2O_5 (K. a. F.).—7. From phenyl *o*-tolyl ketone, MnO_2, and H_2SO_4Aq (Behr a. Dorp, *B.* 6, 753; 7, 16).—8. By acting on *o*-bromo-benzyl bromide dissolved in ether with Na and oxidising the product (anthracene) with CrO_3 (Jackson a. White, *Am.* 2, 390).—9. By action of water on 'anthraquinone chloride' $C_{14}H_8Cl_2O$, obtained by passing chlorine into phenyl *o*-tolyl ketone at 110° (Thörner a. Zincke, *B.* 10, 1479).

Preparation.—Anthracene is dissolved in glacial acetic acid; $K_2Cr_2O_7$ or CrO_3 is added; the liquid is then heated to 100°, the acetic acid is distilled off and the anthraquinone ppd. by water. Large quantities are prepared by oxidising anthracene (100 kilos.) with $K_2Cr_2O_7$ (150 kilos.) sulphuric acid (200 kilos.) and water (2,000 kilos.).

Properties.—Yellow needles (by sublimation). Insol. water, v. sl. sol. alcohol, sl. sol. benzene. Not attacked by alcoholic KOH at 200°; or by cold Br.

Reactions.—1. *Bromine* at 100° forms di-bromo-anthraquinone (*q. v.*).—2. HI and P form anthranol and anthracene dihydride.—3. Heated with *zinc dust* to dull redness it is reduced to anthracene.—4. *Zinc dust* and aqueous NaOH give oxanthranol, $C_6H_4{:}(C_2H_2O_2){:}C_6H_4$ (*q. v.*): when alkyl iodides are added alkyl oxanthranols are got. When stronger soda is used and the alkyl iodide is not added until the reduction is complete, alkyl-hydro-anthranols (*v.* HYDRO-ANTHRANOL) are got (Liebermann, *A.* 212, 100).—5. *Zinc dust* and aqueous NH_3 give dihydro-oxanthranol, $C_6H_4{:}(C_2H_4O_2){:}C_6H_4$.—6. PCl_5 diluted with PCl_3 at 200° forms chlorinated anthraquinones (Graebe a. Liebermann, *A.* 160, 121).—7. *Potash-fusion* at 250° forms potassium benzoate.

Constitution.—The formation of anthraquinone from phthalyl chloride (*q. v.*) and benzene might be thought to indicate the formula

$C_6H_4\langle{}^{CO}_{C\,=\,C_6H_4}\rangle O$. This formula is open to several objections:—(*a*) the group $C_6H_4{:}C$ is unknown; (*b*) it represents a lactone which should be converted by KOH into an oxy acid: (*c*) anthraquinone reacts with hydroxylamine while phthalide and its derivatives do not (E. v. Meyer, *J. pr.* [2] 29, 139, 496; V. Meyer, *B.* 17, 818). There remains the formula

$C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_4$, which agrees with that of anthracene $C_6H_4\langle{}^{CH}_{CH}\rangle C_6H_4$ and must therefore be adopted. Bromo-phthalic acid, benzene, and $AlCl_3$ give bromo-benzoyl-benzoic acid, $CO_2H.C_6H_3Br.CO.C_6H_5$, in which it is evident that the carbonyls are *o* to one another. Conc. H_2SO_4 condenses this acid to bromo-anthraquinone, whence potash-fusion forms an oxy-anthraquinone from which phthalic (not oxy-phthalic) acid can be obtained by nitric acid. Hence the two carbonyls are *o* to one another in both benzene nuclei (Pechmann, *B.* 12, 2125).

Derivatives of anthraquinone are described as CHLORO-ANTHRAQUINONE, BROMO-ANTHRAQUINONE, OXY-ANTHRAQUINONE, OXY-METHYL-ANTHRAQUINONE, METHYL-ANTHRAQUINONE.

ANTHRAQUINONE CARBOXYLIC ACID $C_{15}H_8O_4$ *i.e.* $C_6H_4{:}(C_2O_2){:}C_6H_3CO_2H$. [282°–284°]. Obtained by boiling methyl-anthracene (Weiler, *B.* 7, 1186; O. Fischer, *B.* 7, 1196; Liebermann, *A.* 183, 166; Japp a. Schultz, *B.* 10, 1051), methyl-anthraquinone (Hammerschlag, *B.* 11, 82), or anthracene carboxylic acid [280°] (Liebermann a. v. Rath, *B.* 8, 248), with CrO_3 and HOAc, or the compound $C_{19}H_{14}O$ (obtained by action of conc. H_2SO_4 on amyl-oxanthranol) with CrO_3 and H_2SO_4 (Liebermann, *A.* 212, 97).

Properties.—Compact yellow prisms (from alcohol); yellow needles (by sublimation); v. sl. sol. HOAc, benzene, and alcohol, v. sol. acetone. Decomposed by heat into CO_2 and anthraquinone. The sodium salt is insol. NaOHAq.

Salts.—BaA'_2(?Aq) needles, v. sol. hot water.—CaA'_2(?Aq).

The following derivatives are got from the acid obtained by oxidising methyl-anthraquinone (Liebermann a. Glock, *B.* 17, 888).

Ethyl ether A'Et: [147°], needles, easily soluble in alcohol.

Chloride $C_{14}H_7O_2.COCl$: [147°], needles, very stable towards water.

Amide $C_{14}H_7O_2.CO.NH_2$: [above 280°], needles, very stable compound.

Anilide $C_{14}H_7O_2.CO.NHPh$: [260°], needles, very sparingly soluble in most solvents.

(γ)-Anthraquinone carboxylic acid. [285°]. From the corresponding anthracene carboxylic acid (Liebermann a. Bischof, *B.* 13, 49). Yellow needles (from glacial HOAc). Its alkaline solutions do not fluoresce. Its barium salt is v. sl. sol. water. This acid may be identical with the preceding.

Anthraquinone-di-*m*-carboxylic acid

$\overset{(1)}{C_6H_4}\langle{}^{CO}_{CO}\rangle C_6H_2\overset{(2:4)}{(CO_2H)_2}$. [above 330°]. Formed by oxidation of the corresponding *m*-di-methyl-anthracene. Yellow needles. Nearly insol. water, sl. sol. other solvents. Dissolves in aqueous NH_3 with a red colour; the NH_4 salt crystallises in easily soluble small red warts; its solution gives with $AgNO_3$ a reddish pp. of $A''Ag_2$. By zinc-dust and aqueous NH_3 the acid is reduced to anthracene-*m*-di-carboxylic acid (Elbs a. Günther, *B.* 20, 1364).

Anthraquinone-di-carboxylic acid

$\overset{(1)}{C_6H_4}\langle{}^{CO}_{CO}\rangle C_6H_2\overset{(3:4)}{(CO_2H)_2}$. [340°]. Formed by oxidation of di-methyl-anthraquinone [183°] by HNO_3 (1·2) at 220°. Yellow needles. Scarcely sol. water, sl. sol. most other solvents. Dissolves in aqueous NH_3 with a red colour. On heating it loses H_2O, giving the anhydride. By zinc-

dust and aqueous NH_3 it is reduced to anthracene-di-carboxylic acid [345°]. The solution of the NH_4 salt gives pps. with $CaCl_2$, $Pb(OAc)_2$, and $AgNO_3$.

Anhydride $C_6H_4.C_2O_2.C_6H_2<{CO \atop CO}>O$: [290°]; sublimes in small yellow needles (Elbs a. Eurich, *B.* 20, 1362).

ANTHRAQUINONE-OXIM $C_6H_4<{C(NOH) \atop CO}>C_6H_4$.

Formed by heating anthraquinone with hydroxylamine hydrochloride and alcohol at 180° (Goldschmidt, *B.* 16, 2179). Red crystalline powder. Sublimes without melting above 200°. Dissolves in H_2SO_4 with an intense yellow colour.

ANTHRAQUINONE SULPHONIC ACID $C_{14}H_8SO_5$ *i.e.* $C_6H_4:(CO)_2:C_6H_3.SO_3H$. Formed together with the disulphonic acid by heating anthraquinone (1 pt.) with H_2SO_4 ($2\frac{1}{2}$ pts.) at 260°. Also from diamido-anthraquinone sulphonic acid by diazo reaction; and from *o*-benzoyl-benzoic acid and fuming H_2SO_4 (Liebermann, *A.* 160, 131; *Suppl.* 7, 805; v. Perger, *J. pr.* [2] 19, 218).

Properties.—Yellow scales, v. sol. water and alcohol, v. sl. sol. H_2SO_4 and ether.

Reactions.—1. Fused with *potash* it forms alizarin, oxy-anthraquinone, and benzoic, *p*-oxy-benzoic and protocatechuic acids.—2. HI and P form anthracene sulphonic acid and its dihydride.—3. Anthracene sulphonic acid is also produced by *sodium-amalgam*, and by *zinc-dust* and *ammonia*.—4. *Ammonia* at 190° forms amido-anthraquinone.—5. *Distillation of the sodium salt* produces, besides small quantities of anthraquinone and oxyanthraquinone, chiefly a compound $C_{28}H_{14}O_6$ which melts far above 300°. This compound forms minute reddish-yellow needles (from glacial HOAc), sl. sol. HOAc, toluene, phenol, and aniline, v. sl. sol. alcohol. At a high temperature it may be sublimed. It is insol. alkalis, but forms a crimson solution in conc. H_2SO_4. Distilled with zinc dust it yields anthracene. Fused with potash it gives alizarin. Its constitution is perhaps $C_6H_4:(CO)_2:C_6H_3O.C_6H_3O:(CO)_2:C_6H_4$. Chromic acid oxidises it to colourless $C_{14}H_6O_4$, [296°], possibly $C_6H_4:(CO)_2:C_6H_2O_2$. This forms transparent plates, insol. aqueous alkalis, v. sl. sol. boiling benzene, sl. sol. acetic acid, m. sol. aniline. It may be sublimed. Alcoholic KOH forms a violet solution decolorised by shaking with air. Distillation with zinc dust produces anthracene (A. G. Perkin a. W. H. Perkin, jun., *B.* 18, 1723; *C. J.* 47, 682).

Salts.—BaA'_2 aq: small leaflets, sl. sol. water.—CaA'_2 2aq: sl. sol. water.—NaA' aq: white leaflets, sl. sol. water.

Chloride $C_{14}H_7O_2.SO_2Cl$. [193°]. Light yellow plates; sol. benzene and acetic acid, v. sl. sol. alcohol and ether. Converted by di-methyl-aniline into the sulphone $C_{14}H_7O_2.SO_2.C_6H_4NMe_2$. [171°].

Amide $C_{14}H_7O_2.SO_2NH_2$. [261°]. Long yellow needles; almost insoluble in alcohol, chloroform and CS_2.

Anilide $C_{14}H_7O_2.SO_2NHPh$. [198°]. Long prisms; sol. alcohol and acetic acid.

Additional References.—Liebermann, *A.* 212, 42; *B.* 12, 189, 1293, 1597; McHoul, *B.* 13, 692.

(α)-Anthraquinone disulphonic acid $C_{14}H_6O_2(SO_3H)_2$. When anthraquinone (1 pt.) is heated with fuming H_2SO_4 ($2\frac{1}{2}$ pts.) at 170°, or when dichloro-anthracene or di-bromo-anthracene is similarly treated, a mixture of (α) and (β) disulphonic acids is got. The salts of the (α) acid are less soluble and less crystalline than those of the (β) acid. The (α) acid is converted by potash-fusion into anthraflavin (di-oxy-anthraquinone), oxy-anthraquinone sulphonic acid, and flavopurpurin (tri-oxy-anthraquinone).

Salts.—Na_2A'' 7aq.—BaA'' aq.—PbA'' aq.

(β)-Anthraquinone di-sulphonic acid. Prepared as above. Potash-fusion produces iso-anthraflavin (di-oxy-anthraquinone) and iso-purpurin (tri-oxy-anthraquinone). The sodium salt heated with NH_3Aq at 180° produces $C_{14}H_5(OH)(NH_2)(SO_3H)$ (Bourcart, *Bl.* [2] 33, 264).

Salts.—Na_2A'' 4aq.—BaA'' 2aq.—PbA'' aq.

χ-Anthraquinone-disulphonic acid $C_{14}H_8O_8S_2$ *i.e.* $C_6H_3(SO_3H):(CO)_2:C_6H_3.SO_3H$. Prepared by oxidation of (β)-anthracene-di-sulphonic acid. On fusion with KOH it first gives chrysazin (di-oxy-anthraquinone) and then oxychrysazin (tri-oxy-anthraquinone).

Salts.—Na_2A'' 4aq: yellow prisms.

(ρ)-Anthraquinone-disulphonic acid $C_{14}H_8O_8S_2$ *i.e.* $\left[3\ {1 \atop 2}\right]$ $C_6H_3(SO_3H)(CO)_2C_6H_3SO_3H$ $\left[{1 \atop 2}\ 6\right]$. Prepared by oxidation of (α)-anthracene-disulphonic acid. On fusion with KOH it first gives anthrarufin (di-oxy-anthraquinone) and then oxy-chrysazin. Salts.—Na_2A'' 5aq: yellow leaflets, sol. water.

References.—Graebe a. Liebermann, *A.* 160, 134; *B.* 3, 636; 7, 805; Liebermann a. Dehnst, *B.* 12, 1288; Perkin, *C. N.* 22, 37; *A.* 158, 323; Schunck a. Roemer, *B.* 9, 379; 10, 1821.

ANTHRAQUINONE CHLORIDE *v.* ANTHRAQUINONE, *Formation* 9.

ANTHRARUFIN *v.* *Di*-OXY-ANTHRAQUINONE.

ANTHROL $C_{14}H_{10}O$ *i.e.* $C_6H_4(C_2H_2)C_6H_3OH$.

Formation.—1. From oxy-anthraquinone and HI.—2. By fusing anthracene sulphonic acid with potash.

Preparation.—Crude sodium anthraquinone sulphonate (1 pt.) is heated on a water bath for a few hours with $1\frac{1}{2}$ pts. of zinc-dust and 7 pts. of conc. ammonia; the anthracene sulphonate thus obtained is fused with NaOH. Leaflets or needles (from dilute alcohol). Insol. water, v. sol. alcohol, acetone, or ether. Decomposes at 200°. Insol. in NH_3Aq, soluble in KOHAq or baryta-water, forming a yellow solution with green fluorescence. Its alcoholic solution shows a violet fluorescence. Conc. H_2SO_4 gives a yellow solution, turned blue by heat. A drop of fuming HNO_3 added to its solution in glacial acetic acid gives a transient green colour. Its alcoholic solution reduces warm $AgNO_3$.

Acetyl derivative [198°]. Microscopic leaflets. Difficultly soluble in cold acetic acid, easily in C_6H_6. CrO_3 in HOAc converts it into the acetyl derivative of oxy-anthraquinone.

Ethyl derivative [146°]. Needles.

Methyl derivative [c. 178°].

References.—Liebermann a. Hörmann, *B.* 12, 589; L. a. Hagen, *B.* 15, 1427; L. a. Bollert, *B.* 15, 226; L., *A.* 212, 26, 49.

Isomerides have been described by Linke, *J. pr.* [2] 11, 227.

ANTHROL-SULPHONIC ACID $C_{14}H_8(OH)(SO_3H)$. Formed by careful fusion of anthracene-di-sulphonic acid with KOH.

Salts.—A'Na: crystals sl. sol. cold water.—A'_2Ba: plates or needles (Schüler, *B.* 15, 1808).

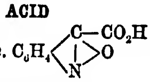
ANTHROPIC ACID. Shown by Heintz (*P.* 84, 238; 87, 233) to be a mixture of palmitic and stearic acids.

ANTHROPOCHOLIC ACID $C_{18}H_{28}O_4$2aq. [145°]. $[\alpha]_D$ 50°. The cholic acid of human bile. The bile is extracted with alcohol; evaporated; extracted with dry alcohol, and the pp. (probably a mixture of sodium glyco-, and tauro-, anthropocholates) is decomposed by boiling with baryta-water (Bayer, *H.* 3, 293).

Properties.—Groups of prisms, insol. water, v. e. sol. alcohol, v. sol. ether, m. sol. chloroform. Lævorotatory. Fusion changes it into an amorphous dyslysin $C_{18}H_{26}O_3$.

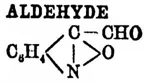
Salts.—KA': v. e. sol. water.—BaA'_2 (? Aq): silky plates, sl. sol. water.

ANTHROXANIC ACID

$C_8H_5NO_3$ *i.e.*  (?)

[191°]. Obtained by oxidation of anthroxanic aldehyde with dilute $KMnO_4$ (Schillinger a. Wleügel, *B.* 16, 2224). White felted needles. Sol. acetone and hot water, v. sl. sol. cold water, sl. sol. alcohol, ether, and benzene. Strong acid. On reduction with $FeSO_4$ and NH_3 it yields isatic acid.

ANTHROXANIC ALDEHYDE

$C_8H_5NO_2$ *i.e.*  (?)

[73°]. Obtained by heating a solution of *o*-nitro-(β)-oxy-cinnamic acid in an equal weight of acetic acid to 100° for a few hours, diluting the product with water, neutralising with $CaCO_3$, distilling with steam, and extracting the distillate with ether. Long yellowish needles. Sublimable. Volatile with steam. Easily soluble in hot water and in most other solvents except ligroine.

The addition of zinc-dust to the dilute ammoniacal solution produces a reddish-violet colouration. It combines with bisulphites and reddens fuchsin-sulphurous acid. With aniline it yields a crystalline anilide which melts at about 40° (Schillinger a. Wleügel, *B.* 16, 2222).

DI-ANTHRYL-FORMAMIDINE *v.* ANTHRAMINE, *reaction* 3.

ANTIARIN $C_{14}H_{20}O_5$2aq (?). [221°]. Poisonous substance in the milky juice of *Antiaris toxicaria* or Upas Antjar, used to poison arrows (Mulder, *A.* 28, 304; Ludwig a. de Vry, *Z.* 1869, 351; Pelletier a. Caventou, *A. Ch.* 26, 57).

ANTIMONIDES. — Binary compounds, or rather alloys, of Sb with more positive metals. Most of these bodies are of somewhat vague compositions; some occur as minerals (*v.* ANTIMONY, *Combinations*, No. 10).

ANTIMONY. Sb. (*Antimonium*, or *Stibium metallicum; Regulus antimonii*). At. w. 120. Mol. w. probably 120, *v.* Biltz a. Meyer, *B.* 22, 725. [about 425°] (between 1090° and 1450°) (Carnelley a. Williams, *C. J.* 35, 566). S.G. 6·71 to 6·86; $^{c.15°}_{4°}$, 6·697 (Schröder, *J.* 1859. 12) S.G. (melted) 6·53 to 6·65 (Playfair a. Joule, *C. S. Mem.* 3, 57). S.H. (0°–100°) ·0495 (Bunsen *P.* 141, 1); ·0523 (Kopp, *A. Suppl.* 3, 66); (0°–33°) ·049; (−21° to 0°) ·048; (−75° to −21°) ·047 (Pebal a. Jahn, *W.* 27, 584). C.E. (cub. 0°–100°) ·003161 (Matthiessen, *P.* 130, 50); (lin. 40°) ·00001152 (Fizeau, *C. R.* 68, 1125). T.C. (Ag = 100) 4·03 (Lorenz, *W.* 13, 422). E.C. (Hg at 0° = 1) 2·05 at 0°, 1·42 at 100° (Lorenz, *l.c.*). Chief lines in spectrum, 6128·5, 6078, 6003·5 (Thalén, *A. Ch.* [4] 18, 243). Crystallises in rhombohedra, approaching cubes (Marx, *S.* 59, 211); isomorphous with As, Bi, and Te.

Occurrence.—Native; but chiefly as sulphide Sb_2S_3 (*Stibnite*), and as double sulphide with PbS, CuS, Ag_2S, NiS, &c.; as oxide in small quantities; in various iron ores; in ferruginous mineral waters; in some gas coals; in certain river sands (Campbell, *P.M.* [4] 20, 304; 21, 318).

Preparation.—The sulphide is fused, to separate gangue, and roasted in air; the oxide thus produced is reduced by heating with charcoal or coal. Or the sulphide is reduced by charcoal or by iron. The crude metal (16 parts) is purified by fusion with dry Na_2CO_3 (2 parts) and Sb_2S_3 (1 part), for an hour in a Hessian crucible; the regulus is separated and again fused for an hour with $1\frac{1}{2}$ parts Na_2CO_3, and this is repeated with 1 part Na_2CO_3 a second time (Bensch, *A.* 5, 20). Or the crude metal is fused with $NaNO_3$ and Na_2CO_3 (details, *v.* Meyer, *A.* 66, 238). Pure Sb is prepared by Dexter (*J. pr.* 18, 449) by fusing dry H_3SbO_4 with lampblack, and then with a little Sb_2O_3. Capitaine (*P.* 100, 563) prepares the pure metal by heating tartar-emetic in a closed crucible. Bongartz (*B.* 16, 1942) digests pure $SbCl_3$ with $(NH_4)_2S$Aq in Pt vessels, electrolyses, fuses with pure Na_2CO_3, treats with dilute HClAq, cleans with sea sand, and dries. Cooke (*P. Am. A.* [2] 5, 1) reduces $NaSbO_3$ by KCN, and fuses the Sb under Sb_2O_3 for several hours. Pure crystalline Sb may be obtained, according to Pfeifer (*A.* 209, 161), by electrolysing a solution of $SbCl_3$ in HClAq containing not more than 7 p.c. $SbCl_3$. Metallic antimony seems to have been known since the end of the 15th century. The sulphide was known to the ancients as *Stibium*.

Properties.—Brittle, hard, silver-white, metal-like; easily crystallised, isomorphous with As and Te, melts easily [425°]; volatilises at bright red heat in open vessel with simultaneous production of Sb_4O_6; scarcely volatilises in absence of air; but slightly volatile *in vacuo* at 292° (Demarçay, *C. R.* 95, 183); may be distilled in H at white heat. Unchanged in air at ordinary temperatures; melted on charcoal before blowpipe and then exposed to stream of air, pure Sb burns easily to Sb_4O_6; if traces of lead or iron are present a yellow or reddish sublimate is produced on burning before blowpipe. By electrolysis of $SbCl_3$ in HClAq, under special conditions, a lustrous silver-like deposit is obtained on the negative electrode; this deposit when dry explodes when rubbed with a hard substance, or when heated to 200°, with formation of clouds of $SbCl_3$; a similar change occurs when the deposit is heated under water to 75°, but at ordinary temperatures it may be rubbed with a hard body under water without change. This so called *explosive antimony* contains $SbCl_3$ varying from 3 to 20 p.c. A similar ex-

plosive substance is obtained by electrolysing $SbBr_3$ in HBrAq, or SbI_3 in HIAq; the former contains 18 to 20 p.c. $SbBr_3$, it explodes at 160°; the latter contains 22 p.c. HI and also SbI_3, it explodes at 160° (Gore, *Pr.* 9, 70 and 304; *ibid. C. J.* [2] 1, 365; Böttger, *J. pr.* 73, 484; 107, 43). According to Böttger (*C. C.* 1875. 674) *explosive antimony* also contains occluded hydrogen.

The atomic weight of Sb has been determined (i.) by analysing and determining V.D. of certain gaseous compounds, particularly $SbCl_3$ and $Sb(CH_3)_3$; (ii.) by measuring the S.H. of Sb; (iii.) by comparing isomorphous compounds of Sb, As, and Bi; (iv.) by analyses of Sb_2S_3 (Schneider, *P.* 98, 293), $SbCl_3$ (Weber, *P.* 98, 455; Dexter, *P.* 100, 563; Dumas, *C. R.* 46, 951; Kessler, *P.* 95, 204, 113, 134), $SbBr_3$ and SbI_3, and by synthesis of Sb_2S_3 (Cooke, *P. Am. A.* [2] 5, 1; 7, 251; 9, 1; *B.* 13, 951) (*comp.* also Kessler, *B.* 12, 1044; Schneider, *J. pr.* [2] 22, 131; and Bongartz, *B.* 16, 1942). Some of the earlier determinations gave the number 122; but the researches of Cooke have established the value 120. The atom of Sb is trivalent in gaseous molecules, $SbCl_3$, $Sb(CH_3)_3$. Antimony combines with oxygen and chlorine with production of heat: $[Sb^2,O^3,3H^2O] = 167,420$, $[Sb^2, O^5, 3H^2O] = 228,780$, $[Sb, Cl^3] = 91,390$, $[Sb, Cl^5] = 104,870$ (*Th.* 2, 240). Antimony is oxidised by strong HNO_3, or by heating with various metallic oxides, *e.g.* MnO_2, PbO_2; hot conc. H_2SO_4 forms $Sb_2.3SO_4$; Sb combines with Cl or Br with production of light. Pure Sb is unacted on by HClAq out of contact with air; in presence of a little HNO_3Aq solution proceeds rapidly (Cooke, *P. Am. A.* [2] 5, 1). Antimony forms three oxides Sb_4O_6, Sb_2O_4, and Sb_2O_5; various compounds corresponding to the first and third are known. Antimony is more metallic than arsenic, whether considered physically or chemically. Hydrated antimonious oxide, $Sb_2O_3.3H_2O (= Sb(OH)_3)$, is known, and reacts as a feeble base; if one-third part of the H is replaced by K the remaining OH groups may be replaced by the residue of tartaric acid, with formation of $Sb.OK.C_4H_4O_6$ (*v.* ANTIMONIOUS OXIDE, *Reactions*, No. 4). Various compounds of Sb_2O_3 with SO_3 (*v.* ANTIMONIOUS OXIDE, *Reactions*, No. 3), and at least one with N_2O_5 are known. A few unstable salts derived from the hypothetical hydrate $SbO.OH (= Sb_2O_3.H_2O)$ are known, so that Sb_2O_3 acts both towards strong acids and strong alkalis as a feeble salt-forming oxide: thus $[2HClAq, 2Sb^{2}O^{3}Aq] = 4,720$; whereas $[2HClAq, 2Na^{2}OAq] = 25,500$ (*Th.* 2, 241). The thio-antimonites are few in number and their stability is decidedly less than that of the thio-arsenites. The compounds of Sb which most decidedly exhibit negative or acidic functions are Sb_2O_5 and Sb_2S_5; the same holds good for As. The haloid compounds of Sb form many well-marked double salts. Many oxyhaloid compounds are also known. SbH_3 does not combine with acids, but compounds of the type SbR_4X where $R = C_nH_{2n+1}$, and X is a halogen or even OH, have been prepared (*v.* ANTIMONY, COMPOUNDS WITH ORGANIC RADICLES). For further discussion of the chemical relations of Sb, *v.* BISMUTH, CHEMICAL RELATIONS OF; and NITROGEN GROUP OF ELEMENTS.

Reactions.—1. *Water* is not decomposed at ordinary temperatures by Sb; but at a red heat it reacts with steam to produce oxide of Sb and H.—2. Dilute *nitric acid* digested with finely powdered Sb forms a compound of Sb_4O_6 with N_2O_5; stronger acid forms chiefly $Sb_2O_5.xH_2O$ and Sb_2O_4.—3. *Sulphuric acid* reacts with Sb only when conc. and hot; SO_2 is evolved, and a compound, or compounds, of Sb_2O_3 with SO_3 produced.—4. By the action of aqueous *sulphurous acid* at 200° in a closed tube Sb_2S_3 is produced. 5. *Hydrochloric acid* forms $SbCl_3$ when heated with powdered Sb; in absence of air no action occurs (Cooke, *P. Am. A.* [2] 5, 1).—6. *Aqua regia* dissolves Sb forming $SbCl_3$.—7. *Solid phosphoric acid* and carbon heated with Sb form phosphide of Sb.—8. *Alkali nitrates and chlorates* heated with Sb form alkali antimonates and generally also Sb_2O_3.—9. *Alkali sulphates* form Sb_2S_3, alkali sulphide, alkali antimonate, and Sb_2O_3.

Combinations. — 1. With *nascent hydrogen* SbH_3 is formed (*q. v.*). — 2. With *chlorine, bromine*, or *iodine*, the compounds $SbCl_3$ and $SbCl_5$, $SbBr_3$, and SbI_3 are produced (*q. v.*).— 3. With *fluorine* (action of HFAq on Sb_4O_6 and $Sb_2O_5.3H_2O$) SbF_3 and SbF_5 are formed (*q. v.*).—4. Sb combines with *oxygen* to form Sb_4O_6 and Sb_2O_4 (*q. v.*); Sb_2O_5 (*q. v.*) is produced by the action of conc. HNO_3.—5. The sulphide Sb_2S_3 (*q. v.*) may be obtained by heating Sb with *sulphur*; the pentasulphide Sb_2S_5 (*q. v.*) is best produced by decomposing Na_3SbS_4 by an acid.—6. Heated with *selenion* Sb_2Se_3 is formed as a greyish metal-like solid (Berzelius; also Hofacker, *A.* 107, 6; *v.* also Uelsmann, *A.* 116, 124). Sb_2Se_3 fused with Se and an alkali forms alkali seleno-antimonate (*e.g.* Na_3SbSe_4); this compound is decomposed by acids, in absence of air, with ppn. of brown Sb_2Se_5. (Hofacker, *l.c.*). — 7. With *tellurium* (Oppenheim, *J. pr.* 71, 277) Sb forms either iron-grey SbTe, or tin-white Sb_2Te_3 (S.G. of latter $\frac{13°}{} = 6·47–6·51$; Bödeker a. Giesecke). — 8. *Phosphorus* is said to combine with Sb to form a tin-white brittle phosphide containing 15·5 p.c. P (Landgrebe, *S.* 53, 469). By the action of P (in CS_2) on $SbBr_3$ (in CS_2) a red powder, PSb, is obtained (Macivor, *B.* 6, 1362).— 9. Sb combines with *arsenic*, by fusion under boric acid, to form crystalline Sb_2As (Descampes, *C. R.* 86, 1065). The compound Sb_2As_3 occurs native as *allamontite*. — 10. *Antimony* forms *alloys* with many *metals*; they are usually produced by melting together Sb and the specified metal. The alloys with K and Na are produced by fusing Sb with K_2CO_3 (or Na_2CO_3) and C, or by reducing Sb_4O_6 with $KH.C_4H_4O_6$ at high temperatures; they decompose water with evolution of H and separation of Sb; if containing much K or Na they take fire in the air. The alloys of Sb are usually lustrous, hard, and brittle. The alloys with Cu and Sn will be described under those metals. An alloy of *iron* is formed when Sb_2S_3 is reduced with excess of Fe; a mixture of 7 parts Sb and 3 parts Fe heated to whiteness in a charcoal-lined crucible produces a very hard white alloy. *Gold* loses its malleability by the presence of about $\frac{1}{2000}$ of Sb. *Lead* alloys with Sb in all proportions; the lead is hardened; type metal is an alloy of about

17–20 parts Sb with lead and sometimes Bi or Sn (*v.* Lead, alloys of). With *nickel* two alloys are known; NiSb sublimes in prisms; Ni_2Sb occurs as *breithauptite* containing a little Fe and PbS. Two alloys with *silver*, Ag_4Sb and Ag_6Sb, occur native as *antimonial silver*. With *zinc* at least two crystalline alloys of definite composition are known, $SbZn_3$ and $SbZn_2$ (Cooke, *Am. S.* [2] 18, 229; 20, 222).

Many of these alloys are used in manufactures. Antimony compounds are also used in medicine.

Detection.—Most Sb compounds are insoluble in water and in excess of conc. HNO_3Aq, but many dissolve in HClAq, especially if tartaric acid is added; insoluble compounds may be dissolved by fusion with KNO_3 and K_2CO_3 and treatment with HClAq; when Sb compounds are fused with $NaNO_3$ and Na_2CO_3, $NaSbO_3$, insoluble in water, is formed.

In dry way. Heated on charcoal with Na_2CO_3 and KCN, all Sb compounds yield a brittle lustrous metallic bead. In the upper reduction-flame of the Bunsen lamp, Sb compounds give a green colour to the flame; in the oxidation-flame, a white oxide film is obtained (on porcelain) which, moistened with neutral $AgNO_3Aq$ and then blown on with ammoniacal air, gives a black spot (Ag_4O).

In wet way. I. *Antimonious compounds.* (i.) *Sulphuretted hydrogen* pps. orange-red Sb_2S_3 from acidulated solutions, soluble in KOHAq or NaOHAq, less soluble in NH_3Aq, insoluble in NH_4HCO_3Aq, soluble in K_2SAq and $(NH_4)_2SAq$, insoluble in dilute acids, but dissolved by boiling with conc. HClAq. Dilute tartar emetic solution is not ppd. by H_2S, the liquid turns red; conc. solutions are completely ppd. (Schulze, *J. pr.* [2] 27, 320). (ii.) Heated with *gold chloride* solution in presence of HClAq, Au is ppd. along with Sb_2O_5. (iii.) *Caustic and carbonated alkalis* pp. white Sb_4O_6 soluble in KOHAq and NaOHAq; the ppn. is slow and incomplete in presence of tartaric acid. (iv.) *Zinc* pps. Sb as a black powder; in presence of acids and Pt the Sb is deposited on the Pt, and a little SbH_3 is also formed; the deposited Sb is insoluble in cold HClAq, but easily dissolves in HNO_3Aq. (v.) *Zinc and iron powder*, added to a solution of an antimonious compound in conc. NH_4ClAq containing NH_3Aq, ppt. Sb on the Zn without production of any SbH_3; under similar conditions arsenious compounds yield AsH_3. (vi.) *Zinc and dilute H_2SO_4Aq*, in absence of HNO_3Aq, evolve H, mixed with SbH_3, which may be burnt in air with production of Sb_2O_3, or decomposed by heat into Sb and H, or led into $AgNO_3Aq$ whereby silver antimonide is ppd. mixed with Ag, or passed over S in sunshine whereby orange Sb_2S_3 is formed (*v.* Jones, *C. J.* [2] 14, 649; this is a very delicate test; *v.* Marsh's test for arsenic, under Arsenic, Detection of). (vii.) Dissolved in KOHAq, and treated with *silver nitrate*, a brown black pp. is obtained, from which NH_3Aq removes Ag_2O, leaving black Ag_4O.

II. *Antimonic compounds.*—(i.) *Sulphuretted hydrogen* pps. orange-red Sb_2S_5 from acidulated solutions, soluble in KOHAq, in K_2CO_3Aq, in $(NH_4)_2SAq$, and more slowly in NH_3Aq. (ii.) Heated with *hydrochloric acid and potassium iodide*, SbI_3 and I are formed ($Sb_2O_5 + 10KIAq = 2SbI_3Aq + 5K_2OAq + 4I$). As antimony trioxide has no action on KI, this reaction may be used to detect Sb_2O_5 in Sb_2O_3. (iii.) *Gold salts, chromates,* and *permanganates*, are *not* reduced by antimonic compounds; nor is $AgNO_3Aq$ acted on (compare tests (ii.) and (vii.) for antimonious compounds). (iv.) Towards *zinc*, or *iron, and acids*, antimonic compounds behave similarly to antimonious (*v.* Antimonoso-antimonic oxide). Antimony tetroxide Sb_2O_4 gives the reactions both of Sb_2O_3 and Sb_2O_5; an alkaline solution reduces $AgNO_3Aq$ and $AuCl_3Aq$ slowly.

(For details of procedure in cases of suspected poisoning by Sb compounds a manual of toxicology must be consulted, *e.g.* Taylor *On Poisons*, or Taylor's *Medical Jurisprudence.*)

Antimony may be separated (qualitatively) from tin and arsenic by treating the sulphides with conc. $(NH_4)HCO_3Aq$, which dissolves only As_2S_3, then dissolving the SnS (or SnS_2) and Sb_2S_3 in conc. HClAq, boiling off H_2S, ppg. Sb in one portion by Zn, reducing $SnCl_4$ to $SnCl_2$ in another portion by boiling with Cu turnings, and ppg. by $HgCl_2Aq$; or the solution containing $SbCl_3$ and $SnCl_4$ may be diluted and boiled with a slight excess of iron wire whereby Sb is ppd. and $SnCl_4$ is reduced to $SnCl_2$ (Classen, *J. pr.* 93, 477). Sb_2S_3 is completely converted into $SbCl_3$ by dry HCl at ordinary temperatures, whereas SnS is unacted on (Tookey, *J. pr.* 88, 435). A little As in Sb compounds may be detected by fusing with 2 pts. Na_2CO_3 and 4 pts. $NaNO_3$, and dissolving in water, Na_3AsO_4 goes into solution and $NaSbO_3$ remains.

Estimation.—I. Gravimetric methods. Antimonious compounds are ppd. by H_2S in presence of HClAq and tartaric acid, excess of H_2S is removed by CO_2, the pp. of Sb_2S_3 is collected (after boiling for 15–20 mins.; Sharples, *Fr.* 10, 343), on a weighed filter, dried at 100° and weighed; a portion is then dried by heating in a stream of dry CO_2 and again weighed; if a portion of the pp. dried at 100° yields S on treatment with hot conc. HClAq, the pp. contains Sb_2S_5 or free S; in this case the other portion must be heated in dry CO_2 until S is no longer volatilised; the residue is now pure Sb_2S_3 (*v.* also Cooke, *P. Am. A.* 13, 1; 17, 13). Or the pp. of Sb_2S_3 (perhaps mixed with Sb_2S_5 and S) may be converted into Sb_2O_4 by treatment with conc. HNO_3Aq (for details *v.* Bunsen, *A.* 106, 3). Schneider (*P.* 110, 634) decomposes the Sb_2S_3 by HClAq, leads the H_2S into an alkaline solution and determines it by volumetric methods (iodine method, or ppn. by excess of titrated As_2O_3Aq and determination of excess of As_2O_3 by iodine).

II. Volumetric methods. (i.) Antimonious compounds are oxidised to antimonic by iodine in alkaline solutions ($Sb_2O_3 + 4I + 2H_2O = Sb_2O_5 + 4HI$). $NaHCO_3Aq$ is the best alkaline solution; titrated I solution is run in until a blue colour is produced with starch. (ii.) Antimonious compounds are oxidised to antimonic in presence of tartaric acid, by $K_2Mn_2O_8$ solution (attention must be paid to details, *v.* Guyard, *Bl.* 6, 89). For other methods of estimating Sb, especially in presence of As, or of As and Sn *v.* Bunsen, *A.* 106, 3; 192, 317; Clarke, *Am. S.* [2] 49, 48.

References.—In addition to those in the text,

the following older memoirs are important:—Bergmann, *Opusc.* 3, 164; Thénard, *A. Ch.* 32, 257; Proust, *G. A.* 25, 186; Berzelius, *S.* 6, 144; 22, 69; 34, 58; *P.* 20, 365; 37, 163; Berthier, *A. Ch.* [2] 22, 239; 25, 379; H. Rose, *P.* 8, 441; 42, 532; 24, 165; Vauquelin, *S.* 21, 219.

Antimony, acids of, and their salts (compare arts. ACIDS; ACIDS, BASICITY OF; HYDROXIDES). The oxides Sb_2O_4 and Sb_2O_5 are scarcely soluble in water, but each reddens moist blue litmus paper; the oxide Sb_4O_6 is slightly soluble in water, but is without action on litmus. A few feebly marked salts are known which may be regarded as derived from the hypothetical hydrate $Sb_2O_3.H_2O$ ($=SbO.OH$); two sodium salts, so-called *antimonites*, are obtained according to Terreil (*A. Ch.* [4] 7, 380) by dissolving Sb_4O_6 in boiling NaOHAq and allowing to cool (*v. infra*). Two hydrates of Sb_4O_6, viz. $Sb_4O_6.4H_2O$ and $Sb_4O_6.6H_2O$ have been obtained (*v.* ANTIMONIOUS OXIDE); but neither seems to possess acidic properties. The oxide Sb_4O_6 reacts with Na_2CO_3 when the two are fused together, but on adding water Sb_4O_6 is ppd. and NaOH remains in solution. The acid-forming character of Sb_4O_6 is therefore extremely feeble (*v.* further ANTIMONIOUS OXIDE).

No hydrate of Sb_2O_4 is known; but by fusing this oxide with KOH or K_2CO_3, a compound, $Sb_2O_4.K_2O$, insoluble in cold water, is produced; by dissolving this in hot water and adding various metallic compounds, several compounds of Sb_2O_4 with metallic oxides, *e.g.* $Sb_2O_4.CaO$ and $Sb_2O_4.CuO$ (which both occur native as *roméite* and *ammiolite* respectively [? merely mixtures]) are obtained. A solution of Sb_2O_4 in KOHAq (obtained by fusion) is easily decomposed: *e.g.* on boiling and then diluting, Sb_2O_3 is ppd. and $Sb_2O_5.xH_2O$ is then thrown down on addition of acids; on standing in air, without boiling, $KSbO_3$ is produced. The oxide Sb_2O_4 cannot therefore be regarded as a definite anhydride, nor can any acid, or well-marked series of salts, be said to exist corresponding with this oxide (*v.* ANTIMONY, OXIDES OF).

Three hydrates of antimonic oxide are known (*v. infra*): $Sb_2O_5.H_2O$ ($=HSbO_3$), $Sb_2O_5.2H_2O$ ($=H_4Sb_2O_7$), and $Sb_2O_5.3H_2O$ ($=H_3SbO_4$). The first and third may be obtained from $H_4Sb_2O_7.2H_2O$ which is a product of the action of water on $SbCl_5$; dried over H_2SO_4, H_3SbO_4 is obtained, and at higher temperatures $HSbO_3$ is produced (*v.* ANTIMONATES). Several fairly marked salts are known, *antimonates*, derived from $HSbO_3$; two series of *metantimonates* ($M_4Sb_2O_7$ and $M_2H_2Sb_2O_7$) exist (*v. infra*); no salts of the hydrate $Sb_2O_5.3H_2O$ ($=H_3SbO_4$) have been obtained. Antimonates are usually obtained by fusion; aqueous alkalis dissolve the hydrate $Sb_2O_5.H_2O$ without change; some metantimonates are produced from the hydrate $Sb_2O_5.2H_2O$ by the action of alkalis in the wet way. Antimonic oxide is evidently a feebly marked acid-forming oxide. The only definite compounds of Sb hitherto obtained which exhibit acidic characters are then $HSbO_3$ and $H_4Sb_2O_7$.

The following thermal data are given by Thomsen $[Sb^2, O^3, 3H^2O] = 167,420$; $[Sb, O^2, H, H^2O] = 117,890$; $[Sb^2, O^5, 3H^2O] = 228,780$; $[Sb, O^3, H, H^2O] = 145,570$; $[SbO^3H^3, O] = 30,680$.

I. ANTIMONITES.—Two sodium salts are described by Terreil (*A. Ch.* [4] 7, 380): $NaSbO_2.3H_2O$, lustrous octahedral crystals, obtained by dissolving Sb_4O_6 in boiling NaOHAq and allowing to cool; $NaSbO_2.Sb_2O_3.H_2O$, large crystals, insoluble in water, obtained from very concentrated alkaline solutions.

II. ANTIMONOSO-ANTIMONATES.—This name has been given to the compounds of Sb_2O_4 with metallic oxides; it implies that these bodies are compounds of antimonites with antimonates; very little, however, is known of their properties. Two potassium salts $K_2O.Sb_2O_4$ (?$KSbO_3.KSbO_2$), and $K_2O.2Sb_2O_4$ are said to be produced, the former by fusing Sb_2O_4 with KOH or K_2CO_3 and washing with cold water, the latter by the action of a little HClAq on the former. An aqueous solution (the salt dissolves in hot water) of $K_2O.Sb_2O_4$ is said to give pps. with various metallic salts. These salts might perhaps be regarded as derivatives of the hypothetical hydrates $Sb_2O_4.H_2O$ ($=H_2Sb_2O_5$) and $2Sb_2O_4.H_2O$ ($=H_2Sb_4O_9$); but our knowledge of them is almost nil.

III. ANTIMONATES, AND ANTIMONIC ACIDS.—Three hydrates of Sb_2O_5 are known. By ppg. $KSbO_3$Aq by HNO_3Aq, washing the pp. and leaving it for a whole summer, Geuther obtained the hydrate $Sb_2O_5.3H_2O$ ($=H_3SbO_4$) (*J. pr.* [2] 4, 438): at 175° this hydrate gives $HSbO_3$ ($=Sb_2O_5.H_2O$). The hydrate $Sb_2O_5.2H_2O$ ($=H_4Sb_2O_7$) is obtained by adding hot water to $SbCl_5$, and drying the pp. of $H_4Sb_2O_7.2H_2O$ at 100°; it is also produced by decomposing the salts $M_4Sb_2O_7$ by acids: this hydrate is easily decomposed to $HSbO_3$, even by standing in contact with water (Dubrawa, *A.* 186, 110; Conrad, *C. N.* 40, 197). $HSbO_3$ may also be obtained by decomposing $MSbO_3$ by acids, or by oxidising Sb by HNO_3. The hydrate $HSbO_3$ is slightly soluble in water, insoluble in NH_3Aq, and easily soluble in KOHAq; $H_4Sb_2O_7$ is more soluble in water, and dissolves in both NH_3Aq and KOHAq: little is known of the hydrate $Sb_2O_5.3H_2O$. The antimonates belong to the two types $MSbO_3$, and $M_4Sb_2O_7$; the former are usually called antimonates, the latter metantimonates.

Antimonates: investigated by Berzelius, then by Fremy (*A. Ch.* [3] 12, 499; 22, 404), and by Heffter (*P.* 86, 418; 98, 293). These salts are obtained by fusing Sb or Sb_2O_3 with nitrates, or $HSbO_3$ with carbonates, or by double decomposition from the K salts; aqueous alkalis dissolve $HSbO_3$ without change. Some of the K and NH_4 salts are soluble in water, the others are slightly soluble or insoluble. The normal antimonates are converted into acid salts by the action of weak acids (*e.g.* CO_2Aq), they are decomposed by stronger acids with separation of $HSbO_3$; the antimonates are decomposed by fusion with NH_4Cl, the whole of the Sb being volatilised as $SbCl_3$; those which are soluble in water or acids are decomposed by $(NH_4)_2S$Aq, with production of thio-antimonates.

Ammonium antimonate $NH_4SbO_3.2H_2O$; white crystalline powder, insoluble in water, easily decomposed with loss of NH_3: obtained by dissolving $HSbO_3$ in warm NH_3Aq.

Barium antimonate $Ba(SbO_3)_2$; obtained by adding $BaCl_2$Aq to $KSbO_3$Aq; pp. at first is

flocculent but becomes crystalline. By adding $BaCl_2Aq$ to boiling $NaSbO_3Aq$ a flocculent pp. of $Ba(SbO_3)_2.5H_2O$ (air-dried) is obtained.

Potassium antimonates.—The normal salt $KSbO_3$ is obtained by fusing 1 part Sb with 4 parts KNO_3, and washing with hot water; it dissolves after long boiling with water, and is obtained as a mass of white crystals when the solution is evaporated until a crust forms. Another form of this salt is described by Fremy as a gummy mass, obtained by evaporating the foregoing solution nearly to dryness, or more easily by long-continued fusion, either alone or with KOH or K_2CO_3, of the product obtained by melting together 1 part Sb and 4 parts KNO_3. The gum-like salt dried in vacuo is $2KSbO_3.5H_2O$, it is easily soluble in hot water; dried at 160° it leaves $2KSbO_3.3H_2O$ which is changed to the gum-like salt by boiling with water; at a red heat all the water is removed, and the product is gradually changed to the gum-like salt by contact with hot water. When the normal salt is boiled with water, a residue of $2KSbO_3.Sb_2O_5.10H_2O$ is obtained; and a similar salt with $6H_2O$ is produced by the action of CO_2 on the normal salt (Heffter, *P.* 86, 418; *v.* also v. Knorre a. Olschewsky, *B.* 18, 2353).

Sodium antimonates. — The salt $2NaSbO_3.7H_2O$ is obtained similarly to the normal $KSbO_3$; also in octahedra by the action of NaOHAq on Sb_2S_3. $NaSbO_3.3H_2O$ is said to be formed by the action of NaOHAq on Sb_2S_3, filtration, and addition of more NaOHAq (*v.* also v. Knorre a. Olschewsky, *B.* 18, 2353).

Many other antimonates are described by Fremy and Heffter; the chief are the salts $Ca(SbO_3)_2$, $Co(SbO_3)_2$, $Cu(SbO_3)_2.5H_2O$, $Pb(SbO_3)_2$, $LiSbO_3$, $Mg.2SbO_3.12H_2O$, $Hg(SbO_3)_2$, $Sr(SbO_3)_2.6H_2O$, $Sn(SbO_3)_2.2H_2O$ (*v.* also Schiff, *A.* 120, 47; Unger, *Ar. Ph.* [2] 147, 195).

Metantimonates. These salts fall into two classes—normal salts $M_4Sb_2O_7$, and acid salts $M_2H_2Sb_2O_7$; they are formed from the antimonates by addition of metallic oxide or water ($2MSbO_3 + M_2O = M_4Sb_2O_7$; and $2MSbO_3 + H_2O = M_2H_2Sb_2O_7$); conversely the metantimonates lose M_2O (or H_2O) and form $MSbO_3$. The metantimonates as a class are insoluble in water, the alkali salts are crystalline; they are decomposed by acids; they have been chiefly investigated by Fremy (*A. Ch.* [3] 12, 499).

Ammonium metantimonates.—$H_4Sb_2O_7$ dissolves slowly in cold NH_3Aq; a conc. solution on addition of alcohol gives the acid salt $(NH_4)_2H_2Sb_2O_7.5H_2O$; this salt is easily decomposed by heating, either in presence or absence of water, into $(NH_4)SbO_3$. The normal salt has not yet been isolated.

Potassium metantimonates.—By fusing $KSbO_3$ (best the gum-like salt) with about 3 parts KOH, dissolving in water, and crystallising, the salt $K_4Sb_2O_7$ is obtained as deliquescent, easily soluble, crystals. The acid salt $K_2H_2Sb_2O_7.6H_2O$ is produced by decomposing the normal salt by a little water (KOHAq is also produced), or by dissolving $SbCl_3$ in excess of KOHAq, oxidising by $K_2Mn_2O_8Aq$, and crystallising (Reynoso, *A. Ch.* [3] 23, 325); at 200° the dehydrated salt $K_2H_2Sb_2O_7$ is obtained, and at 300° $KSbO_3$ is formed. The acid salt is slightly soluble in cold water, more easily in water at 40°-50°, with gradual production of the gum-like $KSbO_3$; an aqueous solution of this salt precipitates sodium salts. Other metantimonates are described by Fremy (*l.c.*).

Seleno-antimonates.—A few salts are known, derived from the hypothetical seleno-antimonic acid H_3SbSe_4. $Na_3SbSe_4.9H_2O$ forms orange-red tetrahedral crystals, and is obtained by fusing Na_2CO_3, Sb_2Se_3, Se, and C; the salt $Na_3SbS_3Se.9H_2O$ is obtained as yellow tetrahedral crystals by boiling Na_3SbS_4Aq with Se (Hofacker, *A.* 107, 6).

Antimony, alloys of, *v.* Antimony, *Combinations*, No. 10.

Antimony, arsenide of, *v.* Antimony, *Combinations*, No. 9.

Antimony, bromide of. $SbBr_3$. No other bromide is known. Mol. w. 359·28; [90°-94°] (Serullas, *P.* 14, 112). (275°-280°) (Kopp, *A.* 94, 257; Cooke, *P. Am. A.* [2] 5, 72). V.D. 180 (Worcester, *P. Am. A.* [2] 10, 61). S.G. $\frac{23°}{}$ 4·148 (Cooke, *l.c.*); fused $\frac{90°}{0}$ 3·641 (Kopp, *l.c.*). If the vol. of fused $SbBr_3 = 1$ for $d° = 0°$, then the vol. at $t° = 1 + \cdot000576d + \cdot0000013465d^2$, where $d = t° - 90°$ (Kopp, *l.c.*). H.F. solid Sb, gaseous Br,$[Sb,Br^3] = 76,900$ (Guntz, *C. R.* 101, 161).

Formation.—1. By shaking powdered Sb into a retort containing Br and connected with a condenser.—2. By distilling a mixture of Sb sulphate and KBr (Macivor, *C. N.* 29, 179).

Preparation.—1. By adding powdered Sb to a solution of Br in dry CS_2 at 0°, distilling off CS_2, adding powdered Sb, distilling off the $SbBr_3$ and recrystallising it from CS_2 (Cooke, *P. Am. A.* [2] 5, 72; Nicklès, *C. R.* 48, 837).

Properties and *Reactions.*—Deliquescent trimetric crystals; $a:b:c = 1{\cdot}224:1:1{\cdot}064$ (Cooke, *l.c.*); sublimes when heated. Decomposed by water; cold water produces $Sb_4O_5Br_2$, hot water $10Sb_4O_5Br_2.SbBr_3$ (Macivor, *C. N.* 29, 179). The compound $Sb_4O_5Br_2$ is also produced by heating $SbBr_3$ with alcohol to 160° (Macivor, *l.c.*). The action of air and sunlight on $SbBr_3$ in CS_2 produces an oxybromide, probably SbOBr (Cooke, *P. Am. A.* [2] 5, 72). Combines with KCl to form $SbBr_3.3KCl$, which according to Atkinson is identical with $SbCl_3.3KBr$ obtained by action of $SbCl_3$ on KBr in presence of a little water (*C. J.* 43, 290).

Antimony, chlorides of. Sb and Cl combine directly to form two compounds $SbCl_3$ and $SbCl_5$; the former may be gasified, the latter is decomposed by heat at ordinary pressures into $SbCl_3 + Cl_2$ (*v. infra*).

I. Antimonious chloride. $SbCl_3$. Mol. w. 226·11. [73°·2] (Thorpe, *C. J.* 37, 387). (223·5°) (216°, Cooke, *P. Am. A.* [2] 5, 72). S.G. $\frac{73°}{}$ 2·6753 (Thorpe, *l.c.*). S.G. 3·064 (Cooke, *P. Am. A.* [2] 5, 72). V.D. 115·6. V = $1 + \cdot0008054d + \cdot00001032d^2$, where d = degrees above M.P. (73·2°) (Thorpe, *l.c.*). $[Sb,Cl^3] = 91,390$ (Thomsen).

Formation.—1. By dissolving Sb, Sb_2O_3, or Sb_2S_3, in HClAq with a little HNO_3Aq, evaporating, and then distilling.—2. By the action of Cl on Sb_2S_3.—3. By distilling together 1 part powdered Sb with 2 parts $HgCl_2$; or 3 parts Sb_2S_3 with 7 parts $HgCl_2$; or 1 part $Sb_2(SO_4)_3$ with 2 parts dry NaCl.—4. By distilling 2 parts Sb_2O_3 (impure), with 6 parts dry NaCl, 4 parts H_2SO_4, and 2 parts H_2O and changing the

receiver as soon as the distillate begins to solidify on cooling.

Preparation.—1. By passing dry Cl into a retort containing powdered Sb, until most of the Sb is transformed into $SbCl_3$; a little more Sb is then added, the stream of Cl is stopped, and the $SbCl_3$ is distilled off into a dry receiver. Cooke (*P. Am. A.* [2] 5, 72) saturates warm CS_2 with $SbCl_3$ and cools by freezing mixture. A solution of $SbCl_3$ in conc. HClAq (generally prepared by the action of the acid on Sb_2S_3) is used in pharmacy.

Properties.—A colourless, translucent, crystalline, mass. Melted and allowed partially to solidify, or dissolved in hot CS_2 and cooled, trimetric crystals are obtained, $a:b:c=$ 1·263:1:1·09 (Cooke, *P. Am. A.* [2] 5, 72). Very caustic. Soluble in alcohol without change; on heating this solution oxychlorides of Sb (*q.v.*), HCl, and C_2H_5Cl, are formed. It absorbs moisture from the air and forms a clear liquid, from which crystals of $SbCl_3$ are obtained by standing over H_2SO_4.

Reactions.—1. With *water* various oxychlorides are produced ($SbCl_3$ dissolves unchanged in a very little water at ordinary temperatures); if a little cold water is added (about 2 parts to 1 part $SbCl_3$), and the pp. is washed with ether, SbOCl (*q. v.*) is obtained (Peligot, *A.* 64, 280; Sabanajew, *Bl.* [2] 16, 79). When from 5 to 50 parts H_2O are added to 1 part $SbCl_3$, the compound $Sb_4O_5Cl_2$ (*q. v.*) is obtained (Sabanajew, *l.c.*). Other observations point to a varying composition for the product of the mutual action of $SbCl_3$ and H_2O; by continued washing the whole of the Cl may be removed (*v.* Duflos, *S.* 67, 268; Johnston, *J. pr.* 6, 55; Malaguti, *J. pr.* 6, 253; Peligot, *A.* 64, 280; Schneider, *P.* 108, 407; Schäffer, *A.* 152, 314). Thomsen (*Th.* 2, 240) gives these data: $[SbCl^3,Aq]=8,910$ when $Sb_4O_5Cl_2$ is formed, and $=7,730$ when Sb_2O_3Aq and HClAq are formed. According to Williams (*C. N.* 24, 225) boiling water produces $10Sb_4Cl_2O_5.SbCl_3$. Formation of oxychlorides is prevented by tartaric acid.—2. *Antimonious oxide* dissolves in boiling $SbCl_3$ to form oxychlorides; $SbOCl.7SbCl_3$ is described by Schneider (*P.* 108, 407).—3. *Alcohol* heated with $SbCl_3$ in proportion $C_2H_6O:SbCl_3$ in a closed tube to 160° forms SbOCl; heated to 140° in the proportion $3C_2H_6O:SbCl_3$, $Sb_4O_5Cl_2$ is formed (Schäffer, *A.* 152, 314).—4. Aqueous solution of *sodium thiosulphate* reacts on solution of $SbCl_3$ to form a double compound of Sb_2O_3 and Sb_2S_3, probably $Sb_2O_3.Sb_2S_3$ (*v.* Antimony, oxysulphides of).—5. Boiling $SbCl_3$ dissolves powdered antimony trisulphide, on cooling a crystalline mass of sulphochloride, $SbSCl.7SbCl_3$, is obtained; on washing with alcohol $2SbSCl.3Sb_2S_3$ remains (Schneider, *P.* 108, 407).

Combinations.—1. With *chlorine*, $SbCl_5$ is formed.—2. *Ammonia* forms $SbCl_3.NH_3$ which on warming gives off all its NH_3.—3. By mixing conc. solutions of $SbCl_3$ and *alkaline chlorides* and evaporating, double salts are formed, *e.g.* $2NH_4Cl.SbCl_3$; $2(BaCl_2.SbCl_3).3H_2O$; $3KCl.SbCl_3$; $3NaCl.SbCl_3$. With KBr the salt $SbCl_3.3KBr$ is formed identical with $SbBr_3.3KCl$ obtained by the action of KClAq on $SbBr_3$ (Atkinson, *C. J.* 43, 290).

II. Antimonic chloride $SbCl_5$. Mol. w. unknown; vapour obtained by heating consists of $SbCl_3+Cl_2$. [−6°] (Kämmerer, *B.* 8, 507). S.G. $\frac{20°}{0}$ 2·346 (Haagen, *P.* 131, 117). (79° at 22 mm.; 68° at 14 mm.) (Anschütz a. Evans, *C. J.* 49, 708).

Preparation.—Powdered Sb is heated in a retort in a rapid stream of dry Cl; $SbCl_5$ (and Cl) distils over, and $SbCl_3$ remains. Or melted $SbCl_3$ is saturated with Cl, and distilled in a stream of Cl (or under greatly diminished pressure, Anschütz a. Evans, *C. J.* 49, 708).

Properties.—Colourless, or slightly yellow, liquid, with an offensive smell, fuming in moist air; solidifies at a low temperature ($<-6°$); absorbs moisture from air and changes to a crystalline mass. According to Anschütz a. Evans (*C. J.* 49, 708) $SbCl_5$ may be distilled unchanged at low pressures.

Reactions.—1. Dissolves in a very little *water*; solution over H_2SO_4 deposits crystals of $SbCl_5.4H_2O$. Kept cold by ice, and water added drop by drop in proportion $SbCl_5:H_2O$, $SbOCl_3$ (*q.v.*) is formed (Dubrawa, *A.* 184, 118). Addition of more water produces SbO_2Cl, which is decomposed by hot water, giving $H_4Sb_2O_7.2H_2O$, soluble in HClAq. Decomposition by H_2O hindered by tartaric acid. Thomsen (*Th.* 2, 242) gives the number $[SbCl^5, Aq]=35,200$, when Sb_2O_5Aq and HClAq are formed.—2. Dry *sulphuretted hydrogen* produces white crystals of $SbSCl_3$, which are decomposed by heat into $SbCl_3$ and S_2Cl_2 (Cloez, *J. pr.* 51, 459).—3. Heated in closed tube to 140° with *antimonic oxide*, in proportion $3SbCl_5:Sb_2O_5$, Sb_3OCl_{13} and $Sb_3O_4Cl_7$ (*q. v.*) are produced (Williams, *C. J.* [2] 10, 122).—4. With *phosphorus trichloride* (in $CHCl_3$) reacts to form $PCl_5.SbCl_3$, and $SbCl_3$ (*v. Combinations*).—5. Chlorinates many *carbon compounds*, *e.g.* $CHCl_3$ to CCl_4, C_2H_4 to $C_2H_4Cl_2$, &c. (*v.* Chloro-compounds). 6. With *nitrogen tetroxide* forms $SbCl_5.NOCl$ (Weber, *P.* 123, 347).

Combinations.—1. With *ammonia* forms brown $SbCl_5.6NH_3$ which may be sublimed unchanged.—2. With *hydrocyanic acid* forms white crystals of $SbCl_5.3HCN$, which volatilise with partial decomposition under 100°, and are decomposed by H_2O (Klein, *A.* 74, 85).—3. With gaseous *cyanogen chloride* forms $SbCl_5.CNCl$ (Klein, *l.c.*).—4. Combines with some *non-metallic chlorides* to form double compounds which usually deliquesce in air and are decomposed by heat; the more important are $SbCl_5.PCl_5$ (Weber, *P.* 125, 78; Köhler, *B.* 13, 875); $SbCl_5.POCl_3$, $SbCl_5.SeCl_4$ and $SbCl_5.SCl_4$ (Weber, *l.c.*); and $SbCl_5.SeOCl_2$ (Weber, *P.* 125, 325).—5. Also combines with $C_6H_5PCl_4$ to form $SbCl_5.C_6H_5PCl_4$ (Köhler, *B.* 13, 1626).—6. Combines with various *alcohols*, and with *ether* (Williams, *C. J.* [2] 15, 463).

Antimony, fluorides of. Sb_2O_3 dissolves in HFAq to form SbF_3; $Sb_2O_5.xH_2O$ dissolves in HFAq to form SbF_5. Neither has been gasified, so that mol. ws. are unknown.

I. Antimonious fluoride SbF_3 [abt. 292°] (Carnelley, *C. J.* 33, 275).

Preparation.—(Berzelius, *P.* 1, 34; Dumas, *A. Ch.* [2] 31, 435; Flückiger, *A.* 84, 248).—1. By dissolving Sb_2O_3 in HFAq, evaporating at 70°–90° and crystallising.—2. By distilling Sb with HgF_2.

Properties.—White, trimetric, octahedral

deliquescent, soluble in H_2O without decomposition.

Reactions.—1. Solution in *water* on evaporation yields an oxyfluoride (composition unknown).—2. *Deliquesced* SbF_3 pressed between paper gives $2SbF_3.Sb_2O_3$ ($=3SbOF.SbF_3$), which is decomposed by heating into SbF_3 and Sb_2O_3.

Combinations.— With *alkali fluorides* to form double compounds, SbF_3 combining with MF, 2MF, or 3MF, where M = K, Na, &c. These compounds are best obtained by dissolving Sb_2O_3 and M_2CO_3 in the proper proportions in HFAq, and evaporating. The principal compounds are $SbF_3.2NH_4F$; $SbF_3.2KF$, $SbF_3.KF$; $SbF_3.2LiF$; and $SbF_3.2NaF$ (*v.* Flückiger, *A.* 84, 248).

II. Antimonic fluoride, SbF_5. Obtained by Berzelius, investigated more fully by Marignac (*A.* 145, 239).

Preparation.—By dissolving hydrated Sb_2O_5 in HFAq, and evaporating.

Properties.—A gum-like amorphous mass, decomposed by heat; very slowly decomposed, in solution, by H_2S.

Combinations.—With the *alkali fluorides*, to form double compounds, which are easily soluble in water, crystallise badly, and yield oxyfluorides when evaporated in aqueous solutions, *e.g.* $SbOF_3.NaF$ from $SbF_5.2NaF$ (Marignac, *A.* 145, 239). These solutions are very slowly decomposed by H_2S, KOHAq, and K_2CO_3Aq. The more important compounds are $SbF_5.NH_4F$, $2(SbF_5.2NH_4F).H_2O$; $SbF_5.KF$, $SbF_5.2KF.2H_2O$; $SbF_5.NaF$.

Antimony, haloid compounds of. SbF_3, SbF_5; $SbCl_3$, $SbCl_5$; $SbBr_3$; SbI_3, (?SbI_5). Only $SbCl_3$ has been gasified and V.D. determined; $SbCl_5$ is decomposed by heat. The formulæ of the trihaloid salts are probably molecular, *v.* Antimony, fluorides of, chlorides of, bromides of, iodides of; *v.* also art. Haloid compounds.

Antimony, hydride of (*v.* also art. Hydrides). SbH_3. (*Antimoniuretted hydrogen*; *Stibine*.) Only one hydride of Sb, SbH_3, is certainly known; and this has not been obtained except mixed with much H. Marchand (*J. pr.* 34, 381) described a black powder obtained by electrolysing conc. NH_4ClAq with a rod of Sb as neg. and a thick Pt wire as pos. electrode. When a powerful battery was used, gas came off which burnt in the air; the powder was supposed to be a solid hydride of Sb, and the gas a spontaneously inflammable hydride (*v.* also Ruhland, *S.* 15, 418). But Marchand's results were not confirmed by Böttger (*J. pr.* 68, 372), who obtained only the ordinary products of the electrolysis of NH_4ClAq, viz. H, NH_3, and N chloride. Wiederhold (*C. C.* 1864. 995) described a graphite-like powder obtained by the action of dilute HClAq on an alloy of 1 part Sb with 5 parts Zn; after drying at 100° this powder gave off ·001 p.c. H at 200° (Sb_2H requires ·004). The gaseous hydride is almost certainly SbH_3 (*v.* especially Jones, *C. J.* [2] 14, 647), but it has not yet been obtained free from H.

Preparation.—By treating an alloy of 2 parts Zn and 1 part Sb (Capitaine, *B. J.* 20, 89), or 3 Zn and 2 Sb (Lassaigne, *B. J.* 22, 104), with dilute H_2SO_4Aq. Schiel (*A.* 104, 223) decomposes an alloy of Sb with K with dilute HClAq. Humpert (*C. C.* 1865. 863) treats conc. $SbCl_3Aq$ with Na amalgam. Jones obtained a gas containing about 4 p.c. SbH_3 by dropping conc. solution of $SbCl_3$ in conc. HClAq on to granulated Zn; the gas was partially decomposed as it was formed (*C. J.* [2] 14, 641).

Properties.—A colourless gas, with nauseating smell and intensely disagreeable taste, slightly soluble in H_2O but decomposed by long contact into Sb and H; easily decomposed by heat; burns in air to Sb_4O_6 and H_2O, or in limited supply of air to Sb, Sb_4O_6, and H_2O; decomposed by electric sparks into Sb and H. The gas obtained by reacting on an alloy of 2 parts Sb with 3 parts Zn with dilute H_2SO_4Aq, and collecting the first portions only, solidified at −91·5°, and decomposed, with separation of Sb, between −65° and −56° (Olszewski, *M.* 7, 371).

Reactions.—1. With *oxygen* and heat, explosion occurs and formation of Sb_4O_6 and H_2O; the same products are obtained by burning in air. — 2. Decomposed by *chlorine*, *bromine*, or *iodine*, with formation of $SbCl_3$, $SbBr_3$, or SbI_3; passed through a hot tube containing a little I, an orange-yellow or brown ring of SbI_3 is formed (Husson, *J. pr.* 106, 314).—3. Passed over *sulphur* in sunshine, or at temperatures over 100°, orange-coloured Sb_2S_3 is formed; very minute quantities of the gas may be thus detected ($2SbH_3 + 6S = Sb_2S_3 + 3H_2S$) (Jones, *C. J.* [2] 14, 649).—4. Decomposes *sulphuretted hydrogen* in sunshine forming Sb_2S_3 ($2SbH_3 + 3H_2S = Sb_2S_3 + 6H_2$) (Jones, *l.c.*).—5. With *antimonious chloride*, Sb and HCl are formed.—6. Easily oxidised by *nitric acid*.—7. Decomposed by *aqueous potash or soda* with separation of a black powder (? $SbOH_3$ or ? Sb_2O, *v.* Jones, *l.c.*; also Dragendorff, *Fr.* 5, 200) which is at once dissolved on shaking in air.—8. With aqueous *silver nitrate* the whole of the Sb is ppd. (as Ag_3Sb mixed with Ag, Lassaigne, *B. J.* 22, 104; *v.* also Jones, *l.c.*).

References. — Thompson, *B. J.* 18, 135; Pfaff, *P.* 40, 339; Simon, *P.* 42, 369; Vogel, *J. pr.* 13, 57; Meissner a. Hankel, *J. pr.* 25, 243.

Antimony, hydroxides of. Several compounds of Sb, H, and O are known; some of them are probably best regarded as hydrated oxides; others react as acids, especially $HSbO_3$ and $H_4Sb_2O_7$; *v.* Antimony, Acids of (*v.* also arts. Acids and Hydroxides).

Antimony, iodide of. SbI_3. Only one iodide of Sb is known with certainty; van der Espt (*Ar. Ph.* [2] 117, 115) asserts that SbI_5 is produced by heating 1 part Sb with 5 parts I, or by leading SbH_3 into I in alcohol; but as SbI_3 is known to be produced by such processes the existence of the pentiodide is extremely doubtful (comp. Pendleton, *C. N.* 48, 97). Mol. w. 499·62. [167°] (Cooke, *P. Am. A.* [2] 5, 72). (401° at 760 mm.) (Cooke, *P. Am. A.* [2] 7, 251). V.D. 252 (Worcester, *P. Am. A.* [2] 10, 61). S.G. hexagonal $^{24°}$ 4·848, monoclinic $^{24°}$ 4·768 (Cooke, *l.c.*). H.F. solid Sb, gaseous I, $[Sb, I^3] = 45{,}400$ (Guntz, *C. R.* 101, 161).

Formation.—1. By the action of powdered Sb on I in CS_2.—2. By the action of SbH_3 on I.—3. By subliming together Sb_2S_3 with 3I in a globe (Schneider, *P.* 109, 609).

Preparation.—Powdered Sb is added little by little to I, with gentle heating, until no further action occurs; the SbI_3 is then separated by sublimation in H or CO_2.

Properties. — Red crystals, which melt on

heating and volatilise in red vapours; soluble in boiling CS_2, and boiling benzene, but separates out on cooling; almost insoluble in $CHCl_3$; soluble in HIAq. Exists in three forms: (*a*) hexagonal ruby-red crystals, by crystallisation from CS_2, M.P. = 167°, $a:c = 1:1{\cdot}37$; (*b*) trimetric greenish-yellow crystals, by subliming the hexagonal form at temperatures not above 114°; at 114° the change is sudden, the external form of the hexagonal crystals is preserved but each crystal is found to consist of a mass of trimetric crystals; heated above 114° the hexagonal form is reproduced; (*c*) monoclinic crystals ($a:b:c$ = 1·6408:1: ·6682) obtained by exposing a solution of SbI_3 in CS_2 to direct sunlight; at 125° they are changed into the hexagonal form (Cooke, *P. Am. A.* [2] 5, 72).

Reactions.—1. *Water* decomposes SbI_3 with production of HIAq, which dissolves part of the SbI_3, and oxyiodide of Sb (*q. v.*).—2. *Aqueous alkalis and alkali carbonates* produce Sb_2O_3 and alkali iodide (Serullas, *J. Ph.* 14, 19).—3. Conc. *sulphuric acid or nitric acid* separates I.—4. *Alcohol or ether* partly dissolves SbI_3 and partly changes it to yellow oxyiodide (Macivor, *C. J.* [2] 14, 328).—5. *Chlorine* forms $SbCl_3$ and ICl (Macivor, *l.c.*).—6. *Antimony trisulphide* reacts with molten SbI_3 to form SbSI; this sulphoiodide is obtained as a lustrous brown-red powder by treating the fused mass with dilute HClAq; it is decomposed by H_2O and KOHAq; boiled with H_2O and ZnO the oxysulphide Sb_2OS_2 is formed (Schneider, *P.* 110, 147).

Combinations.—Dissolves in aqueous solutions of the *iodides of the alkali metals*, on evaporation double compounds are obtained. These compounds are soluble in HClAq, $H.C_2H_3O_2Aq$, and $H_2.C_4H_4O_6Aq$; they are decomposed by H_2O, yielding Sb oxyiodide; CS_2 dissolves out SbI_3. The following salts are described by Schaeffer (*P.* 109, 611): $2SbI_3.3KI.3H_2O$; $2SbI_3.3NaI.12H_2O$; $4SbI_3.3NH_4I.9H_2O$; $SbI_3.BaI_2.9H_2O$. Nicklès (*C. R.* 51, 1097) describes two series of compounds $MI.SbI_3.2H_2O$, and $MI.SbI_3.H_2O$ where M = K, Na, or NH_4, obtained usually by the action of I on Sb in presence of saturated MIAq; these salts are isomorphous with corresponding double salts of Bi.

Antimony, livers of. This name is applied to the impure double sulphides obtained by heating Sb_2S_3 with various metallic sulphides, more especially with the alkali and alkaline earth sulphides. These bodies are obtained either by fusing Sb_2S_3 with K_2S, &c., with K_2SO_2 &c. and C, or by dissolving Sb_2S_3 in K_2SAq, &c. The behaviour of aqueous solutions varies according to the relative quantities of Sb_2S_3 and alkali sulphide employed; if not more than 2 parts Sb_2S_3 are used to 1 part alkali sulphide, the product is wholly soluble in water; if more Sb_2S_3 is used the product is partly, or wholly, insoluble (because of production of antimonate and Sb_4O_6 *v.* ANTIMONIOUS SULPHIDE, *Reactions*, No. 15). Solutions of these bodies dissolve Sb_2S_3 on boiling; the Sb_2S_3 pps. again on cooling; they readily absorb O from the air, forming antimonate and thioantimonate (*v.* ANTIMONIOUS SULPHIDE, *Reactions*, No. 15). Addition of alkali bicarbonates pps. thioantimonite.

Antimony, oxides of. Three oxides are known: Sb_4O_6, Sb_2O_4, and Sb_2O_5; only the first of these has been gasified; the molecular weights of the others are not known. The pentoxide acts as an anhydride; the two others are feebly salt-forming whether they react with strong acids or strong alkalis (*v.* ANTIMONY, ACIDS OF). Marchand (*J. pr.* 34, 381) described an oxide, Sb_3O_2, said to be obtained by the electrolysis of a solution of cream of tartar; but Böttger (*J. pr.* 68, 372) failed to obtain anything except antimonic acid by repeating the experiments.

I. ANTIMONIOUS OXIDE Sb_4O_6 (*Antimonious acid*). Mol. w. 575·76. S.G. trimetric 5·5 to 5·6, regular octahedra 5·1 to 5·2 (Terreil, *C. R.* 58, 1209). V.D. 286·5 (at abt. 1550°; Meyer, *B.* 12, 1284). S.H. ·0927 (18° to 100°; Neumann, *P.* 126, 123). C.E. (40° cub., *Senarmontite*) ·00005889 (Fizeau, *A. Ch.* [4] 8, 335).

Occurrence.—Native; as *Antimony bloom* in trimetric prisms, as *Senarmontite* in octahedra.

Formation.—1. By heating Sb in a loosely covered crucible, and then raising the temperature, when Sb_4O_6 mixed with a little Sb_2O_4 sublimes on to the crucible cover.—2. By treating Sb with dilute HNO_3Aq and washing thoroughly with water and then with very dilute Na_2CO_3Aq (Rose, *P.* 53, 161).—3. By fusing Sb with KNO_3 and $KHSO_4$ and boiling fused mass in water (Preuss, *A.* 31, 197).—4. By washing the white pp. obtained by adding H_2O to $SbCl_3$ with dilute KOHAq and then with H_2O.—5. By adding excess of NH_3Aq to hot $KSb.C_4H_4O_7Aq$, heating pp. for a short time in contact with the liquid, collecting, and washing.

Preparation.—1. 3 parts finely powdered Sb are heated with 7 parts conc. H_2SO_4; the crude Sb sulphate is treated repeatedly with hot water, and then with very dilute Na_2CO_3Aq, and the oxide is collected and dried.—2. 1 part powdered Sb is heated, so long as an action occurs, with 4 parts HNO_3Aq, S.G. 1·2, and 8 parts H_2O; the nitrate of Sb is treated as the sulphate in 1.

Properties.—A white, more or less crystalline, powder (regular octahedra); very slightly soluble in water, fairly soluble in glycerine (Köhler, *D. P. J.* 258, 520); becomes yellow when heated, but white again on cooling; melts at a dark red heat, and crystallises on cooling. Volatilises rapidly about 1550° (Meyer, *B.* 12, 1284). Insoluble in HNO_3Aq and H_2SO_4Aq; dissolves easily in HClAq and $H_2.C_4H_4O_6Aq$; also in KOHAq and NaOHAq, from these solutions Sb_4O_6 is ppd. on cooling (Mitscherlich, *A. Ch.* [2] 33, 394), but according to Terreil the pp. is an antimonite (*A. Ch.* [4] 7, 380). Sb_4O_6 is formed in trimetric prisms ($a:b:c$ = ·394:1:1·414) by burning Sb or Sb_2S_3 in air, by heating oxychloride (obtained by adding H_2O to $SbCl_3$) with H_2O to 150° (Debray, *C. R.* 58, 1209), or by rapidly subliming the octahedral crystals (Terreil, *C. R.* 62, 302); Sb_4O_6 is formed in regular octahedra by subliming at a dark red heat. Both forms are obtained by saturating hot Na_2CO_3Aq with Sb_2O_3 or $SbCl_3$ and allowing to cool (Mitscherlich, *P.* 15, 453); or by passing a slow stream of dry air through a porcelain tube containing Sb, the tube being heated at first only where the Sb is, but after a few hours also at the point where the prisms might condense, after about 12 hours prismatic crystals are found near the Sb, prisms

mixed with octahedra further on, and octahedra only near the end of the tube (Terreil, *l.c.*). Sb_4O_6 is isodimorphous with As_4O_6 (*q. v.*). According to Guntz (*C. R.* 98, 303) the change of prismatic Sb_4O_6 to octahedral is attended with production of 1200 gram units of heat per 576 grms. Sb_4O_6 changed.

Reactions.—1. Heated in air or *oxygen*, Sb_2O_4 is formed.—2. Conc. hot *nitric acid* oxidises to Sb_2O_4 and Sb_2O_5; it dissolves in *cold fuming HNO₃* and forms $Sb_4O_6.N_2O_5$ (Peligot, *C. R.* 23, 709).—3. Treated with *fuming sulphuric acid*, small lustrous crystals are obtained, which, after drying for six months in contact with burnt clay have the composition $Sb_4O_6.2SO_3$; by treating these crystals with H_2O the salt $Sb_4O_6.SO_3$ is obtained (Peligot, *l.c.*). Schultz-Sellac (*B.* 4, 13) describes the salt $Sb_2.3SO_4$ ($=Sb_4O_6.6SO_3$) as long lustrous needles obtained by evaporating solutions of Sb_4O_6 in fairly conc. H_2SO_4Aq; this salt is unchanged in dry air, but gives off SO_3 on heating, and is decomposed by water. $Sb_2(SO_4)_3$ is also formed by dissolving Sb_2S_3 in hot conc. H_2SO_4Aq (Hensgen, *R. T. C.* 4, 401) (*v.* SULPHATES).—4. Sb_4O_6 dissolves in solution of *potassium-hydrogen tartrate*, forming the salt $C_4H_4KSbO_7$, which is probably the K salt of the acid $Sb.C_4H_4O_6.OH$ (*v.* Clarke and Stallo, *B.* 13, 1787).—5. Sb_4O_6 acts as a reducing agent towards salts of silver, gold, &c. (*v.* ANTIMONY, DETECTION OF, *Antimonious compounds*).—6. Sb_4O_6 does not directly combine with *water*, but two hydrates have been prepared:—(*a*) $Sb_2O_3.2H_2O$, by adding $CuSO_4Aq$ to Sb_2S_3 dissolved in KOHAq until the filtered liquid gives a white pp. ($Sb_2O_3.2H_2O$) on addition of an acid (Fresenius; *v.* also Schaffner, *A.* 51, 182); (*b*) $Sb_2O_3.3H_2O$, a white powder which begins to lose water above 150°, obtained by the spontaneous decomposition of an aqueous solution of the acid $H.C_4H_4SbO$, obtained by decomposing $(C_4H_4SbO_7)_2Ba$ by the proper quantity of H_2SO_4Aq (Clarke a. Stallo, *B.* 13, 1793).—7. Dissolves in boiling *antimonious chloride* to form oxychlorides; $SbOCl.7SbCl_3$ is described by Schneider (*P.* 108, 407).

II. ANTIMONIC OXIDE Sb_2O_5 (*Antimonic acid*). Mol. w. unknown. S.G. 3·78 (Playfair a. Joule, *C. S. Mem.* 3, 83).

Preparation.—By dissolving powdered Sb in aqua regia, or conc. HNO_3Aq, evaporating to dryness, and heating [not above 275°] (Geuther, *J. pr.* [2] 4, 438; Dubrawa, *A.* 186, 110).

Properties.—Citron-yellow powder; insoluble in water, but reddens moist blue litmus paper; loses O at 300° (Geuther, *l.c.*) giving Sb_2O_4; soluble in conc. HClAq, slightly soluble in conc. KOHAq.

Reactions.—1. Heated with *antimony* or *antimony sulphide*, Sb_2O_4 is formed.—2. Heated in *chlorine*, $SbCl_3$ and Sb_2O_4 are produced.—3. Heated with *ammonium chloride*, is completely volatilised.—4. Reacts with *alkaline carbonates* on fusion, with evolution of CO_2 (*v.* further ANTIMONY, DETECTION OF, *Antimonic compounds*).—5. Hydrates are not produced by the direct action of water, but indirectly the three compounds, $Sb_2O_5.3H_2O$, $Sb_2O_5.2H_2O$, and $Sb_2O_5.H_2O$, have been obtained (*v.* ANTIMONY, ACIDS OF, ANTIMONATES). Forms many compounds with WO_3 and MoO_3 (*v.* Gibbs, *C. N.* 48, 155; *Am.* 7, 209 and 313).

III. ANTIMONOSO-ANTIMONIC OXIDE Sb_2O_4 (*Antimony tetroxide*). Mol. w. unknown. S.G. 4·074 (Playfair a. Joule, *C. S. Mem.* 3, 83); 6·5 (Boullay, *A. Ch.* [2] 43, 266). S.H. (23°-99°) ·09535 (Regnault, *A. Ch.* [3] 1, 129).

Occurrence.—Native, as *Antimony-ochre.*

Preparation.—1. By heating Sb_4O_6 in air.—2. By oxidising Sb, Sb_4O_6, or Sb_2S_3, by conc. HNO_3Aq, evaporating to dryness, and strongly heating.

Properties.—White powder, becoming yellow on heating; has not been melted or volatilised; insoluble in water, but reddens moist blue litmus paper; very slightly acted on by acids.

Reactions.—1. Heated with *solution of cream of tartar*, $Sb_2O_5xH_2O$ remains and solution contains $C_4H_4KSbO_7$.—2. Solution in HClAq dropped into *water*, is decomposed into Sb_4O_6 and Sb_2O_5.—3. Heated with *antimony* Sb_4O_6 is formed.—4. With *molten potash* forms $K_2O.Sb_2O_4$ (*v.* ANTIMONY, ACIDS OF; ANTIMONOSO-ANTIMONATES); solution of this in water slowly reduces $AgNO_3Aq$ and $AuCl_3Aq$. Sb_2O_4 reacts as a compound of Sb_2O_3 and Sb_2O_5 ($=Sb_4O_8$); it is sometimes regarded as antimonyl antimonate $(SbO)SbO_3$, derived from $HSbO_3$.

Antimony, oxybromides of. Two oxybromides are obtained by the action of H_2O on $SbBr_3$, viz. $Sb_4O_5Br_2$ and $10Sb_4O_5Br_2.SbBr_3$. SbOBr is probably formed by the action of sunlight on $SbBr_3$ in CS_2 (*v.* ANTIMONY, BROMIDE OF).

Antimony, oxychlorides of. At least six compounds are known; SbOCl, $SbOCl.7SbCl_3$, $Sb_4O_5Cl_2$, and $10Sb_4O_5Cl_2.SbCl_3$, obtained from $SbCl_3$; SbO_2Cl, and $SbOCl_3$, from $SbCl_5$.

When $SbCl_3$ is added to a little water, SbOCl is obtained (sometimes mixed with $SbCl_3$). This oxychloride seems to exist either as a white amorphous powder, or as monoclinic crystals isomorphous with SbOI (Cooke, *P. Am. A.* [2] 5, 72); the crystals are best obtained by using 10 pts. $SbCl_3$ and 17 pts. H_2O, allowing to stand for a day or two, pressing, and washing with ether (Sabanajew, *Bl.* [2] 16, 79); the amorphous powder is best prepared by adding 3 pts. H_2O to 1 pt. $SbCl_3$, filtering at once, drying over H_2SO_4, and washing with ether. Crystalline SbOCl is also obtained by heating $SbCl_3$ with C_2H_6O (in ratio $SbCl_3$:C_2H_6O) in a closed tube to 160° (Schäffer, *A.* 152, 314). By the action of much water on $SbCl_3$ (5 to 50 parts to 1 part $SbCl_3$ according to Sabanajew, *l.c.*) the oxychloride $Sb_4O_5Cl_2$ is obtained as an amorphous powder, which becomes crystalline on standing. To prepare the crystalline forms it is best to use 30 parts of cold water, or 3 parts of water at 60° to 70° (in the latter case allowing the pp. to remain a few hours before collecting); there are some differences in the forms of the two sets of crystals (Sabanajew, *l.c.*). Crystals (trimetric Schäffer, *A.* 152, 314; monoclinic, Cooke, *P. Am A.* [2] 5, 72) of $Sb_4O_5Cl_2$ are also obtained by heating $SbCl_3$ with C_2H_6O (in ratio $SbCl_3$:$3C_2H_6O$) to 140°-150° (Schäffer, *l.c.*). The compound $Sb_4O_5Cl_2$ is also produced by the action of alcohol on SbOCl (Schneider, *P.* 108, 407); and also by heating dry SbOCl ($5SbOCl = Sb_4O_5Cl_2 + SbCl_3$; Sabanajew, *l.c.*).

The product of the action of much H_2O on $SbCl_3$ is known as *powder of Algaroth*; the composition varies according to temperature, quan-

tity of water, and quantity of HCl in the solution of $SbCl_3$ used (comp. Duflos, *S.* 67, 268; Johnston, *J. pr.* 6, 55; Malaguti, *J. pr.* 6, 253; Peligot, *A.* 64, 280).

According to Williams (*C. N.* 24, 224) the action of hot water on $SbCl_3$ produces $10Sb_4Cl_2O_5.SbCl_3$; Williams also describes two oxychlorides obtained by heating Sb_2O_5 with $SbCl_3$ (Sb_2O_5:$3SbCl_3$) to 140° in a closed tube; Sb_3OCl_{13} M.P. = 85°, and $Sb_3O_4Cl_7$ M.P. = 97·5°.

Cooke (*P. Am. A.* [2] 5, 72) describes another oxychloride $Sb_8O_{11}Cl_2$; and Schneider (*P.* 108, 407) two others, $SbOCl.7SbCl_3$ and $2SbOCl.Sb_2O_3$.

According to Thomsen (*Th.* 2, 240) the heat of formation of $Sb_4O_5Cl_2$ from $SbCl_3$ and Aq is 8910 gram-units (*v.* also Guntz, *C. R.* 98, 512). By dropping the calculated quantity of very cold water on to $SbCl_5$, Dubrawa (*A.* 184, 118) obtained $SbOCl_3$ ($SbCl_5 + H_2O = SbOCl_3 + 2HCl$); this oxychloride is a yellowish, somewhat crystalline, mass, soluble in alcohol; it deliquesces to a yellow liquid, from which needle-shaped crystals separate in dry air. When heated it melts and decomposes (probably to $SbOCl + Cl_2$). It is decomposed by Na_2CO_3Aq ($2SbOCl_3 + 3Na_2CO_3Aq = 6NaClAq + 2O + 3CO_2 + Sb_2O_3$).

Antimony, oxyfluoride of. $3SbOF.SbF_3$ obtained by deliquescence of SbF_3 (*v.* ANTIMONY, FLUORIDES OF).

Antimony, oxyiodides of. $Sb_4O_5I_2$ and SbOI. $Sb_4O_5I_2$ is obtained as light yellow crystals by evaporating a solution of $SbCl_3$ in KIAq, adding H_2O and evaporating again. The composition of the oxyiodide obtained by the action of H_2O on SbI_3 varies according to the conditions of its preparation; by pouring SbI_3 in HIAq into hot H_2O, $Sb_4O_5I_2$ is obtained (*v.* Macivor, *C. J.* [2] 14, 328). By the action of air and sunlight on SbI_3 in CS_2 both oxyiodides are formed, production of SbOI proceeding rapidly (Cooke, *P. Am. A.* [2] 5, 72). When SbOI is heated in a current of an inert gas to 150°, SbI_3 begins to sublime, and at 200° is given off rapidly; no further change occurs till 350° is reached, when SbI_3 again sublimes and crystals of Sb_2O_3 remain (Cooke, *P. Am. A.* [2] 5, 72). By the action of HClAq, HNO_3Aq, or H_2SO_4Aq, on SbOI, I is separated.

Antimony, oxysulphides of. Various oxysulphides of Sb, or more probably mixtures of Sb_2S_3 and Sb_2O_3, were formerly used in pharmacy. The compound $Sb_2O_3.2Sb_2S_3$ occurs native as *antimony blende* (*v.* H. Rose, *P.* 3, 452). The oxysulphide Sb_2OS_2 is obtained as a red-brown powder by boiling SbSI (*v.* ANTIMONY, IODIDE OF) with ZnO and H_2O (Schneider, *P.* 110, 147); also by the action of $Na_2S_2O_3Aq$ on $SbCl_3$ in HClAq (Böttger, *C. C.* 1857. 333). A compound of Sb_2S_3 and Sb_2O_3 is much used as a brilliant crimson-red pigment; it is probably $Sb_2O_3.2Sb_2S_3$ (= $3Sb_2OS_2$), (*v.* Böttger, *l.c.*; Wagner, *J.* 1858. 235; Kopp, *C. C.* 1859. 945).

Antimony, phosphides of, *v.* ANTIMONY, *Combinations*, No. 8.

Antimony, selenides of, *v.* ANTIMONY, *Combinations*, No. 6.

Antimony, seleno-acid of, *v.* SELENO-ANTIMONATES, p. 286.

Antimony, sulphides of. Two sulphides are known, Sb_2S_3 and Sb_2S_5; neither has been gasified, and therefore mol. w. of neither is known. Unger (*Ar. Ph.* [2] 147, 193) supposed he had obtained a disulphide, Sb_2S_2, by the action of NaOHAq on Sb_2S_3; but the existence of this Sb_2S_2 is very doubtful. Sb_2S_3 is a feebly marked salt-forming sulphide, *e.g.* it dissolves in NaOHAq to form $Na_2Sb_2S_4$ (*v.* ANTIMONY, THIO-ACIDS OF). Sb_2S_5 is a distinctly salt-forming sulphide; the thio-antimonates (*q. v.*) are well-marked salts. The trisulphide, Sb_2S_3, occurs native; the pentasulphide does not.

I. ANTIMONIOUS SULPHIDE (*Antimony trisulphide, Mineral Kermes,* &c.) Sb_2S_3 [low red heat]. S.G. (*stibnite*) 4·51–4·75; (amorphous) 4·15; (fused, by direct union of Sb and S) 4·892 (Ditte, *C. R.* 102, 212). S.H. (23°–99°) ·08433 (Regnault, *A. Ch.* [3] 1, 129; *v.* also Neumann, *P.* 23, 1). Two forms are known; crystallised (trimetric; a:b:c = ·985:1:1·0117) and amorphous.

Occurrence.—Native as *Stibnite* or *Antimony glance*, crystallised in trimetric prisms, usually containing P, As, Fe, and Cu.

Preparation.—(*a*) Crystallised: by gradually heating to redness, in a covered crucible, a mixture of 13 parts of finely powdered Sb well mixed with 5 parts pure S; then fusing for some time under a layer of NaCl; cooling, powdering, mixing with a little S, and again fusing under NaCl. (*b*) Amorphous: by boiling 4 parts KOHAq, S.G. 1·25, and 12 parts H_2O, with one part crude Sb_2S_3, out of contact with air for some time, adding 50 parts boiling H_2O, filtering quickly, and decomposing the solution by dilute H_2SO_4Aq; the pp. is collected, boiled with very dilute H_2SO_4Aq, washed with cold water, digested with aqueous tartaric acid (to remove any Sb_2O_3), again washed with cold water, pressed, and dried at a low temperature. Cooke (*P. Am. A.* [2] 5, 1) dissolves Sb in large excess of HNO_3Aq (S.G. 1·35), keeping the temperature as low as possible, neutralises with NaOHAq, dissolves in large excess of $H_2C_4H_4O_6Aq$, pps. by H_2S in an atmosphere of CO_2, collects and washes pp. and dries below 210°. The amorphous sulphide is also produced by melting crystalline Sb_2S_3 in a glass tube, and after a time throwing it into a large quantity of cold water (Fuchs, *P.* 31, 578). An impure Sb_2S_3, containing Sb_2O_3, known as *Kermes*, is prepared for commercial purposes by heating crude antimony sulphide with aqueous alkalis or alkaline carbonates.

Properties. —(*a*) Crystalline: grey-black trimetric prisms; melts easily. (*b*) Amorphous: prepared by ppn., is a reddish-brown, loose, powder which marks paper with a brownish streak; prepared by melting and suddenly cooling the crystalline Sb_2S_3, it is a hard greyish mass; melted and cooled slowly it yields the crystalline form; heated to 210°–220° it becomes grey (Cooke, *P. Am. A.* [2] 5, 1). Both forms of Sb_2S_3 are insoluble in water, and in NH_3Aq, dissolve in KOHAq, in HClAq, and very slowly in tartaric acid. They may be distilled unchanged in a stream of N.

Reactions.—The products of the reactions of crystalline and amorphous Sb_2S_3 are, in almost every case, the same; the actions usually proceed more rapidly with the amorphous than with the crystalline form. 1. Boiled with *water*, is partially decomposed to Sb_4O_6 and H_2S (De Clermont a. Frommel, *C. R.* 87, 330; Lang, *B.* 18, 2714).—2. Heated in *hydrogen*, Sb is formed.—

3. *Calcined in air*, Sb_4O_6, or Sb_2O_4, and SO_2 are produced.—4. Heated in *chlorine*, $SbCl_3$ and S_2Cl_2 result.—5. Aqueous *hydrochloric acid* forms $SbCl_3$ and H_2S; after a time the action stops, but if the H_2S is removed the whole of the Sb_2S_3 is decomposed (*v.* Lang, *B.* 18, 2714; also Berthelot, *C. R.* 102, 22).—6. *Conc. nitric acid* oxidises to nitrate and sulphate of Sb mixed with S.—7. *Aqua regia* forms $SbCl_3$, H_2SO_4, and S.—8. Dilute solutions of *sulphuric acid* have no action on crystalline Sb_2S_3, but slowly evolve H_2S from amorphous Sb_2S_3; conc. H_2SO_4Aq evolves SO_2, separates S, and forms $Sb_2(SO_4)_3$ (Hensgen, *R. T. C.* 4, 401).—9. Fused with at least 17 parts *nitre*, $KSbO_3$ is formed, with Sb sulphate; with less than 17 parts nitre, Sb_2O_3 is sometimes formed in addition to the other products, or a part of the Sb_2S_3 remains unoxidised and combines with K_2S formed to produce a thio- salt.—10. Melted with excess of *lead oxide*, Sb_2O_3, SO_2, (and Pb), are formed.—11. Melted with *potassium cyanide*, Sb is produced, along with KCNS and a compound of Sb_2S_3 and K_2S.—12. *Iron, zinc*, and many other *metals* reduce Sb_2S_3, when heated with it, forming Sb and a metallic sulphide; metals whose sulphides are basic (*e.g.* K) generally combine with part of the Sb_2S_3 to form thio- salts.—13. Many *easily reduced metallic oxides* when heated with Sb_2S_3 form Sb_2O_4 and SO_2.—14. Many *metallic sulphides* combine when heated with Sb_2S_3 with production of double compounds; several of these double compounds occur native, *e.g.* $Sb_2S_3.PbS$; $Sb_2S_3.Cu_2S$; $Sb_2S_3.3Ag_2S$; &c.—15. *Alkali sulphides* combine with Sb_2S_3 either when heated in the solid state or in solution; the compounds produced are generally known as *livers of antimony*, *q. v.* (*v.* also next reaction); aqueous solutions of these compounds absorb O forming Sb_4O_6, antimonates, and thio-antimonates.—16. *Caustic alkalis* react with Sb_2S_3, when fused together, or when in aqueous solutions, to produce antimonite and thio-antimonite: thus, $4Sb_2S_3 + 4K_2O = 6KSbS_2 + 2KSbO_2$; or $4Sb_2S_3 + 8KOHAq = 3(Sb_2S_3.K_2SAq)$ $[= 6KSbS_2Aq] + Sb_2O_3.K_2OAq$ $[= 2KSbO_2Aq] + 4H_2O$. Addition of HClAq to this solution pps. Sb_2S_3;
($6KSbS_2Aq + 2KSbO_2Aq + 8HClAq =$
$4Sb_2S_3 + 8KClAq + 4H_2O$). If, however, much Sb_2S_3, relatively to the amount of KOH, is used, formation of $KSbS_2Aq$ proceeds, but the $KSbO_2$ being much less soluble pps. along with some oxysulphide and Sb_4O_6 which has not combined with KOH (*crocus of antimony*). The solution of $KSbS_2$ is acted on by air, giving finally antimonate and thio-antimonate ($6KSbS_2Aq + 6O = 4KSbS_3Aq + 2KSbO_3Aq$).—17. *Solutions of carbonated alkalis*, K_2CO_3 and Na_2CO_3Aq, dissolve Sb_2S_3 only on heating; the solutions behave similarly to those obtained by KOHAq and NaOHAq; on boiling in air a pp. of $KSbO_3$ ($Sb_2O_5.K_2O$) combined with Sb_2S_3 is obtained (*Kermes*), and $KSbS_3$ remains in solution. When 1 pt. Sb_2S_3 is fused at a strong red heat with 3 pts. Na_2CO_3, and H_2O is added, a solution containing antimonate and thio-antimonate is obtained, and Sb is ppd. (probably, $10NaSbO_2Aq + 2H_2O = 6NaSbO_3Aq + 4NaOHAq + 4Sb$). The action of alkalis on Sb_2S_3 has been chiefly investigated by Liebig (*A.* 7, 1).

Combinations.—With metallic sulphides to form thio-antimonites (*v. supra*), *q. v.* under ANTIMONY, THIO-ACIDS OF.

Antimonious sulphide; hydrated. The orange-red pp. obtained by passing H_2S into a solution of $SbCl_3$ or C_4H_4KSbO, containing little acid is amorphous hydrated Sb_2S_3, which is fully dehydrated only at 200° (Fresenius; according to Wittstein the pp. contains no chemically combined H_2O, *Fr.* 1870. 262). It behaves towards acids, alkalis, &c. in the same way as amorphous Sb_2S_3. When this pp. is treated with *peroxide of hydrogen*, in presence of NH_3Aq, a portion of it is oxidised to antimonic acid, some of which separates out and some remains in solution as $NH_4.SbO_3$ (Raschig, *B.* 18, 2743).

II. ANTIMONIC SULPHIDE Sb_2S_5 (*Antimony pentasulphide or persulphide, Golden sulphuret of antimony*, &c.). Mol. w. unknown. Not found native. Sb_2S_3 does not directly combine with S; but by heating Sb_2S_3, S, and Na_2CO_3 together, Na_3SbS_4 is formed, from which Sb_2S_5 is obtained by the action of acids.

Formation.—1. By the action of H_2S on $SbCl_5$ in $H_2C_4H_4O_6Aq$, or on $Sb_2O_5.xH_2O$ suspended in water.—2. By decomposing solutions of thio-antimonates by dilute acid.

Preparation.—10 parts crystallised $Na_3SbS_4.9H_2O$ (*q. v.* under ANTIMONY, THIO-ACIDS OF) are dissolved in 60 parts H_2O; the solution is poured (with constant stirring) into a cold solution of 3·3 parts pure H_2SO_4 in 100 parts H_2O; the pp. is washed by decantation, then on a filter, with cold water, as quickly as possible; to remove all traces of acid, the pp. is now digested with a cold solution of 1 part $NaHCO_3$ in 20 parts H_2O for a few days; it is again washed then pressed, and dried in a dark place at a low temperature.

Properties.—A dark-orange powder; insoluble in water; completely soluble in aqueous alkalis; in absence of air, soluble in NH_3Aq, and in aqueous alkali sulphides; soluble in Na_2CO_3 or K_2CO_3Aq, not in $(NH_4)_2CO_3Aq$.

Reactions.—1. *Heated out of contact with air*, Sb_2S_3 and S are formed.—2. Decomposed by boiling with *hydrochloric acid*, giving $SbCl_3$ and H_2S.—3. *Caustic alkalis* dissolve Sb_2S_5, forming antimonate and thio-antimonate.—4. *Carbon disulphide* dissolves out a little S (about 5 p.c., Rammelsberg, *P.* 52, 193). That this is due to a decomposition of Sb_2S_5, and not to the action of CS_2 on admixed S (it has been supposed that the action of CS_2 proves the non-existence of Sb_2S_5), is shown by the fact that much less than S_2 is withdrawn from each Sb_2S_5 by CS_2, and also by the reactions of the Sb_2S_5, especially the solubility in NH_3Aq in which Sb_2S_3 is insoluble, and the insolubility in $(NH_4)_2CO_3Aq$ which dissolves Sb_2S_3.

Combinations.—With alkali sulphides to form thio-antimonates, *q. v.* under ANTIMONY, THIO-ACIDS OF.

Antimony, sulpho-acids of, *v.* ANTIMONY, THIO-ACIDS OF.

Antimony, sulpho- (or thio)- chlorides of. $SbSCl.7SbCl_3$, and $2SbSCl.Sb_2S_3$, obtained by action of Sb_2S_3 on $SbCl_3$; and $SbSCl_3$ obtained by the action of H_2S on $SbCl_5$ (*v.* ANTIMONY, CHLORIDES OF).

Antimony, sulpho- (or thio)- iodides of. $SbSI$; by action of Sb_2S_3 on SbI_3, or of I on Sb_2S_3 (*v.* ANTIMONY, IODIDE OF).

Antimony, tellurides of, *v.* ANTIMONY, *Combinations*, No. 7.

Antimony, thio-acids of. No thio-acids of Sb are known, but a few thio-antimonites, $MSbS_2$ and one M_3SbS_3, and a considerable number of well-marked thio-antimonates, M_3SbS_4, have been prepared. The thio-antimonites may be regarded as derived from the hypothetical acid $HSbS_2$ (= SbS.SH); they correspond in composition with the antimonites $MSbO_2$ and with the meta-thio-arsenites $MAsS_2$. The thio-antimonates may be regarded as derived from the hypothetical acid H_3SbS_4 (= $SbS(SH)_3$); no corresponding antimonates are known ($MSbO_3$ and $M_4Sb_2O_7$ represent the antimonates); the thio-arsenites are represented by three series, one of which (the ortho-series) corresponds with the thio-antimonates.

THIO-ANTIMONITES. A very few of these salts have been prepared. Addition of absolute alcohol to a solution of Sb_2S_3 in NaOHAq pps. amorphous $NaSbS_2$, soluble in water. By heating to 30° equivalents of Sb_2S_3 and NaOH (in conc. solution) copper-coloured $2NaSbS_2.H_2O$ is formed (Unger, *J.* 1871. 325). The silver salt Ag_3SbS_3 is said to be obtained as a grey mass, reddish when powdered, by heating Ag_3SbS_4 out of contact with air (Rammelsberg, *P.* 52, 193). Several minerals may be regarded as thio-antimonites, *e.g.* $PbS.Sb_2S_3$; $Ag_2S.Sb_2S_3$; $Cu_2S.Sb_2S_3$; $FeS.Sb_2S_3$ &c.

THIO-ANTIMONATES M_3SbS_4. Investigated chiefly by Rammelsberg (*P.* 52, 193). Some of these salts are obtained by the action of alkali sulphides on Sb_2S_5; but they are better obtained by acting on Sb_2S_3 with aqueous solutions of alkali sulphides in presence of sulphur, or with aqueous solutions of alkali polysulphides. They are also obtained by fusing Sb_2S_3 with alkali sulphides (or with sulphates and carbon) and sulphur. The decomposition, in air, of alkaline livers of antimony also often yields thio-antimonates (*v.* ANTIMONIOUS SULPHIDE, *Reactions*, No. 15 and 16). The thio-antimonates of the alkali metals are soluble in water, many of the others are insoluble and are obtained from the alkali salts by ordinary double decompositions, the metallic salt solution being added in quantity less than sufficient to decompose the whole of the alkali thio-antimonate. Solutions of thio-antimonates are easily decomposed by acids, even by the CO_2 of the air, with ppn. of Sb_2S_5, and, when exposed to air, of alkali thio-sulphate. The alkali thio-antimonates are not decomposed by heating out of contact with air; the salts of the heavy metals lose S, and give thio-antimonites. The more important thio-antimonates are those of potassium and sodium.

Potassium thio-antimonate. $2K_3SbS_4.9H_2O$; slightly yellow deliquescent crystals; prepared by boiling, for several hours, 1 part S, 6 parts K_2CO_3, 3 parts CaO, and 20 parts H_2O, with 11 parts Sb_2S_3, filtering, and cooling out of contact with air. A salt $K_3SbS_4.KSbO_3.5H_2O$ is obtained, in long white needles, by adding cold conc. KOHAq to Sb_2S_5, filtering from $2KH(SbO_3)_2.5H_2O$ which separates out, and evaporating (*v.* Schiff, *A.* 114, 202).

Sodium thio-antimonate $Na_3SbS_4.9H_2O$ (known as *Schlippe's salt*). Prepared by fusing together 16 parts dry Na_2SO_4, 13 parts Sb_2S_3, and 4–5 parts wood charcoal, dissolving in water, boiling with 2½ parts sulphur, filtering and evaporating; the crystals are washed with very dilute NaOHAq and then with water, and dried quickly at a low temperature. The salt may also be prepared by boiling Na_2CO_3Aq with CaO, Sb_2S_3, and S. Sodium thioantimonate forms large yellowish monometric tetrahedra; it dissolves in 2·9 parts H_2O at 15°, the solution has an alkaline reaction. The crystals are best kept in contact with their mother liquor to which a little NaOHAq is added; they decompose in air, giving Sb_2S_3, Sb_2S_5, Na_2S, Na_2CO_3, and $Na_2S_2O_3$. When the mother liquor from Schlippe's salt is evaporated, crystals of a double salt $Na_3SbS_4.Na_2S_2O_3.20H_2O$ are obtained. Solution of tartar emetic is decomposed by Na_3SbS_4Aq thus; $6C_4H_4KSbO_7Aq + 2Na_3SbS_4Aq =$
$$6C_4H_4KNaO_6 + Sb_4O_6 + Sb_2S_3 + Sb_2S_5.$$
The other thio-antimonates are generally obtained from the sodium salt: the best-marked are $Ba_3(SbS_4)_2.6H_2O$; $Cu_3(SbS_4)_2$; $Pb_3(SbS_4)_2$; $Hg_3(SbS_4)_2$; Ag_3SbS_4; a few others are known (*e.g.* of Cd, Co, Mn, Ni, V, Zn) but they are very easily decomposed, and not many have been obtained in definite forms. M. M. P. M.

ANTIMONY, Compounds with organic radicles.

References.—Löwig a. Schweizer, *A.* 75, 315; Landolt, *J. pr.* 52, 385; 57, 134; 84, 330; *A.* 78, 91; 84, 44; Buckton, *C. J.* 13, 115; 16, 17; Löwig, *A.* 88, 323; 97, 322; *C. J.* 8, 261; Berlé, *J. pr.* 65, 385; Scheibler, *J. pr.* 64, 505; Friedländer, *J. pr.* 70, 449; Cramer, *Pharm. Cent.* 1855, 465; Hofmann, *A.* 103, 357; Strecker, *A.* 105, 306; v. Rath, *P.* 110, 115; Jörgessen, *J. pr.* [2] 3, 342; Le Bel, *Bl.* [2] 27, 444; Michaelis a. Reese, *A.* 233, 42.

Tri-methyl-stibine $SbMe_3$. Mol. w. 167. (81°). S.G. $\frac{15}{}$: 1·523.

Preparation.—An alloy of antimony (4 pts.) and sodium (1 pt.) is mixed with sand and MeI and distilled. MeI and $SbMe_3$ pass over but unite in the receiver to form $SbMe_4I$, which when distilled with an alloy of antimony and potassium in a current of CO_2 gives $SbMe_3$ (Landolt).

Properties.—Liquid, smelling of onions, sl. sol. water; may take fire in air. Takes fire in chlorine. Reduces salts of silver and mercury.

Salts.—Unites directly with non-metals.—$SbMe_3Cl_2$: hexagonal crystals, sl. soluble in water. Formed also from $SbCl_3$ and $HgMe_2$.—$SbMe_3Cl_2SbMe_3O$: octahedra, sol. water.—$SbMe_3Br_2$.—$SbMe_3Br_2.SbMe_3O$: octahedra, sol. water.—$SbMe_3I_2$: formed by heating Sb with MeI at 140°.—$SbMe_3I_2.SbMe_3O$: octahedra.—$SbMe_3S$: scales.—$SbMe_3(NO_3)_2$.—$SbMe_3SO_4$.

Tetra-methyl-stibonium salts. $SbMe_4I$. S. 30 at 23°. From $SbMe_3$ and MeI: six-sided plates. When distilled the vapour ($SbMe_3$ + MeI) takes fire in air.—$SbMe_4.OH$: from moist Ag_2O and the above. Deliquescent alkaline crystals: absorbs CO_2 from air, and expels NH_3 from its salts. Pps. baryta from BaI_2, also the hydrates of Pb, Ca, Cu, Hg, Ag, and Zn; only the last pp. is soluble in excess.—$SbMe_4Cl$: very soluble hexagonal plates; v. sl. sol. ether.—$(SbMe_4Cl)_2PtCl_4$: difficultly soluble orange powder; sl. sol. water, insol. alcohol and ether.—$SbMe_4Br$.—$(SbMe_4)_2S$:

soluble green powder; oxidises rapidly. — $SbMe_4NO_3$ [150°]: crystals, v. sol. water, not decomposed by boiling concentrated H_2SO_4.— $SbMe_4SO_4H$: soluble plates.—$(SbMe_4)_2SO_4$ 5aq.

Di-methyl-stibine sulphides $(SbMe_2)_2S_2$ [c. 100°] and $(SbMe_2)_2S$ are formed by passing H_2S into an ethereal solution of $SbMe_3$ that has been oxidised by exposure to air.

Antimony penta-methide $SbMe_5$. (c. 98°). Formed together with antimony tetra-methide, $(SbMe_4)_2$ (c. 90°), by distilling trimethyl stibine iodide with $ZnMe_2$. Both are oils which do not fume in air.

Methyl-tri-ethyl-stibonium salts $SbMeEt_3I$. S. 50 at 20°. From $SbEt_3$ and MeI. Glassy prisms, sol. alcohol, insol. ether; the solutions are lævorotatory. $HgCl_2$ gives a precipitate of $SbEt_3MeI\,1\frac{1}{2}HgI_2$.—$SbMeEt_3OH$; from moist Ag_2O and the iodide, or from the sulphate and baryta. Pps. metallic salts, the hydrates of zinc and aluminium dissolving in excess.— $SbMeEt_3Cl$: small needles.—$SbMeEt_3IHgI_2$.— $(SbMeEt_3)_2CO_3$: amorphous.—$(SbMeEt_3)_2SO_4$: [100°], deliquescent, shining, bitter crystals.— $(SbMeEt_3)_2C_2O_4$: glassy needles, m. sol. water.— $SbMeEt_3C_2O_4H$: needles, v. sol. water.—The *acetate, formate*, and *butyrate* are crystalline.

Tri-ethyl-stibine $SbEt_3$. Mol. w. 209. (159°). S.G. $\frac{16}{}$: 1·324. V.D. 7·44 (calc. 7·18).

Formation.—1. From $SbCl_3$ and $ZnEt_2$.— 2. From EtI and a mixture of sand with an alloy of Sb and potassium.—3. From $SbCl_3$ and $HgEt_2$.—4. By distilling $SbEt_3I_2$ with Zn.

Properties.—Oil, smelling of garlic, v. sol. alcohol and ether. Takes fire in air; hence it should be kept under water. Decomposes fuming hydrochloric acid with evolution of hydrogen: $SbEt_3 + 2HCl = SbEt_3Cl_2 + H_2$. When slowly oxidised it forms $SbEt_3O$ and $SbEt_3(SbO_2)_2$. Combines directly with S, Se, I, Br, and Cl. Dilute HNO_3 dissolves it, giving off NO and forming $SbEt_3(NO_3)_2$. In all these reactions tri-ethyl-stibine behaves like a metal. An alcoholic solution of $SbEt_3$ shaken with HgO liberates Hg while $SbEt_3O$ remains in the solution.

Tri-ethyl-stibine-oxide $SbEt_3O$.

Formation.—1. From $SbEt_3I_2$ and Ag_2O.— 2. From $SbEt_3SO_4$ and baryta.—3. By slow oxidation of an alcoholic or ethereal solution of $SbEt_3$; $SbEt_3(SbO_2)_2$ is formed at the same time, but this differs from $SbEt_3O$ in being insol. ether.—4. By shaking alcoholic $SbEt_3$ with HgO.

Properties.—A syrup, v. sol. water and alcohol, m. sol. ether; combines with acids and precipitates metals as hydrates from solutions of their salts. If its aqueous solution is free from $SbEt_3(SbO_2)_2$, no pp. is produced by H_2S; otherwise a pp. of $SbEt_3(SbS_2)_2$ is formed. Potassium converts it into $SbEt_3$.

Tri-ethyl-stibine salts.

Chloride.—$SbEt_3Cl_2$. S.G. $\frac{17}{}$: 1·540. Oil, soluble in alcohol. Ppd. by adding HCl to an aqueous solution of the iodide or sulphate. Conc. H_2SO_4 decomposes it, giving off HCl.

Oxy-chloride.—$SbEt_3Cl_2,SbEt_3O$. From the oxy-iodide and $HgCl_2$. Deliquescent solid.

Bromide. — $SbEt_3Br_2$. S.G. $\frac{17}{}$: 1·953. Solidifies at −10°. Insol. water, sol. alcohol and ether. Behaves like a metallic bromide.

Iodide.—$SbEt_3I_2$. [71°]. Formed by heating Sb with EtI at 140°; or by adding iodine to an alcoholic solution of $SbEt_3$ at −15°. Needles (from ether). Unlike the chloride, it is soluble in water. Potassium removes the iodine thus: $SbEt_3I_2 + K_2 = 2KI + SbEt_3$.

Oxy-iodide.—$SbEt_3I_2,SbEt_3O$. Formed by treating the iodide with NH_3; or by mixing the iodide with the oxide $SbEt_3O$.

Sulphide.—$SbEt_3S$. From the oxide and H_2S or from $SbEt_3$ and S. Soluble in water and alcohol. Its aqueous solutions pp. metals as sulphides from their salts.

Nitrate.—$SbEt_3(NO_3)_2$. [63°]. Formed by dissolving $SbEt_3$, or its oxide, in dilute HNO_3. Rhombohedra, soluble in water.

Oxy-nitrate.—$SbEt_3O,HNO_3$. From the oxy-iodide and $AgNO_3$.

Sulphate.—$SbEt_3SO_4$ [100°]. From the sulphide and $CuSO_4$. Small prisms, sol. water and alcohol.

Oxy-sulphate.—$(SbEt_3O)_2H_2SO_4$. From the oxy-iodide and Ag_2SO_4. Gummy mass.

Tetra-ethyl-stibonium salts.

Iodide.—$SbEt_4I$, $1\frac{1}{2}$aq (and $\frac{3}{4}$aq). S. (anhydrous): 19 at 20°. From $SbEt_3$, water, and EtI at 100°. Hexagonal prisms, sol. alcohol and ether.—$SbEt_4I\,\frac{3}{2}HgI_2$.—$SbEt_4I\,\frac{3}{4}HgI_2$.

Hydrate.—$SbEt_4OH$. From moist Ag_2O and the above. Alkaline syrup. Pps. metallic hydrates from salts: stannic oxide and alumina dissolve in excess. Expels NH_3 from its salts.

Chloride.—$SbEt_4Cl$. Hygroscopic needles. Forms compounds with $HgCl_2$ and with $PtCl_4$.

Bromide.—$SbEt_4Br$Aq: needles.

Periodide.—$SbEt_4I_3$.

Nitrate.—$SbEt_4NO_3$: deliquescent needles.

Sulphate.—$(SbEt_4)_2SO_4$: deliquescent mass.

Oxalate.—$(SbEt_4)_2C_2O_4$.

Antimony-penta-ethide $SbEt_5$ (?). (c. 165°). From $SbEt_3I_2$ and $ZnEt_2$.

Tri-isoamyl-stibine $Sb(C_5H_{11})_3$. From an alloy of Sb with K by $C_5H_{11}I$. Fuming liquid, does not take fire in air.

Oxide. $Sb(C_5H_{11})_3O$: insoluble resin, soluble in alcohol.

Salts. — $Sb(C_5H_{11})_3Cl_2$: oil, heavier than water, soluble in alcohol, ppd. by water.— $Sb(C_5H_{11})_3Br_2$: oil. — $Sb(C_5H_{11})_3I_2$: oil. — $Sb(C_5H_{11})_3(NO_3)_2$: [20°] slender crystals, insoluble in water, soluble in alcohol.—$Sb(C_5H_{11})_3SO_4$: oil.

Antimony di-isoamyl $Sb_2(C_5H_{11})_4$ (?). Formed by distilling $Sb(C_5H_{11})_3$. A heavy oil, soluble in alcohol. Does not fume in air, but explodes in oxygen. Its salts are amorphous.

Tri-phenyl-stibine $SbPh_3$. [48°] (above 360°). S.G. $\frac{12}{}$ 1·500. From $SbCl_3$ (1 pt.), chloro-benzene (1 pt.) and Na; benzene being used as diluent. Small quantities of $SbPh_2Cl_3$ and $SbPh_3Cl_2$ are also formed. The benzene deposits crystalline $SbPh_3$; this is warmed with alcohol containing HCl, which dissolves $SbPh_2Cl_3$, and the residual $SbPh_3$ is converted into $SbPh_3Cl_2$ by chlorine. The latter is reduced by alcoholic ammonia and hydrogen sulphide:

$$SbPh_3Cl_2 + H_2S = SbPh_3 + 2HCl + S.$$

Properties.—Colourless triclinic tables $a:b:c$ = ·697 : 1 : ·889. α = 100° 38′. β = 103° 37′. γ = 75° 25′; sl. sol. alcohol, v. e. sol. ether, benzene, glacial HOAc, CS_2, chloroform, and petroleum; insol. water and aqueous HCl. It does not decompose HCl; but it combines directly with

halogens; it reduces cupric, to cuprous, chloride. With mercuric chloride it reacts as follows:

$$SbPh_3 + 3HgCl_2 = SbCl_3 + 3HgPhCl.$$

Fuming HNO_3 forms $SbPh_3(NO_3)_2$.

Salts.—$SbPh_3Cl_2$ [143°]: long thin needles; not affected by water; insol. light petroleum, sl. sol. ether and alcohol, v. sol. benzene and CS_2. —$SbPh_3Br_2$. [216°]. — $SbPh_3I_2$. [153°]; white tables. — $SbPh_3(OH)_2$. [212°]. From the bromide and alcoholic KOH. Amorphous powder, sol. glacial HOAc and reppd. unaltered by water. Insol. ether, v. e. sol. alcohol. Converted by HCl, HBr, or HI into haloid salt.—$SbPh_3(NO_3)_2$. [156°]. Insol. water, sol. alcohol.

Antimony di-phenyl chloride $SbPh_2Cl_3$ aq. [180°]. Obtained as a by-product in preparing $SbPh_3$. Needles, insol. water, sol. hot dilute HCl, v. e. sol. alcohol. Alcoholic NH_3 converts it into $Ph_2SbO(OH)$, a white powder, insol. water, ammonia, alcohol, ether, or Na_2CO_3Aq, but sol. NaOHAq and glacial HOAc.

ANTIPYRINE *v.* *Oxy-di-*METHYL-QUINIZINE.

APHRODÆSCIN. A substance contained in the cotyledons of the horse-chestnut (*v.* ÆSCINIC ACID).

APIÏN. When common parsley (*Apium petroselinum*) is extracted with boiling water the filtrate gelatinises on cooling. The jelly is dried at 100° and extracted with alcohol, and the alcohol poured into water. The operation of dissolving in alcohol and ppg. with water is repeated several times, and the apiin finally crystallised from alcohol, with stirring. Apiin also occurs in parsley seed; if this is boiled with water, apiol distils over, while apiin separates out from the residue.

Properties.—Needles; sl. sol. cold water, v. sol. hot water, separating again as a jelly; v. sol. alcohol; insol. ether. Its solution in boiling water gives a blood-red colour with $FeSO_4$. Gives picric acid with HNO_3; and phloroglucin by potash fusion.

Apigenin $C_{15}H_{10}O_5$. Boiling dilute H_2SO_4 splits up apiin into apigenin and glucose:

$$C_{27}H_{32}O_{16} + H_2O = C_{15}H_{10}O_5 + 2C_6H_{12}O_6.$$

Crystallises in plates (from alcohol). It sublimes near 294°. Sl. sol. hot water, v. sol. alcohol, insol. ether. *Potash fusion* gives phloroglucin, protocatechuic acid, *p*-oxybenzoic acid, and oxalic acid.

References.—Rump, Buchner's *Repert. f. Pharm.* 6, 6; Braconnot, *A. Ch.* [3] 9, 250; v. Planta a. Wallace, *A.* 74, 262; Lindenborn, *B.* 9, 1123; v. Gerichten, *B.* 9, 1121; Whitney, *Ph.* [3] 10, 585.

APIOL $C_{12}H_{14}O_4$. [30°]. (c. 300°). Extracted by alcohol from parsley seeds (v. Gerichten, *B.* 9, 1477). Needles; insol. water. Alcoholic KOH converts it into two crystalline bodies. [54°] and [114°]. The essential oil obtained by distilling parsley seeds with water contains apiol but consists chiefly of a terpene, (160°–164°), S.G. $\frac{12}{}$ ·865, [α] −30·8°. It has a strong smell of parsley. A small quantity of a hydrochloride, [116°], can be got from it.

References.—Löwig a. Weidmann, *P.* 46, 53; v. Gerichten, *B.* 9, 258, 1121, 1477; Pabitzky, *Braunschw. Anzeiger*, A.D. 1754; Blanchet a. Sell; *A.* 6, 301; Martius, *A.* 4, 267; Homolle a. Joret, *J. Ph.* [3] 28, 212; and the references under Apiin.

APO-. Compounds beginning with this prefix are described under the words to which it is prefixed.

APOCYNIN. The root of *Apocynum Cannabium* contains amorphous resinous apocynin, sol. alcohol and ether, v. sl. sol. water, and a glucoside, apocyneïn (Schmiedeberg, *Ph.* [3] 13, 942).

APOPHYLENIC ACID. The methylo-hydroxide of cinchomeronic acid; *v.* PYRIDINE DI-CARBOXYLIC ACID.

APPLES. The artificial essence of apples contains iso-amyl iso-valerate dissolved in rectified spirit (Hofmann, *A.* 81, 87).

APRICOTS. The artificial essence of apricots contains isoamyl butyrate and isoamyl alcohol.

AQUA REGIA *v.* CHLORHYDRIC ACID.

AQUA VITÆ. Alcohol.

ARABIC ACID (Arabin) $C_{12}H_{22}O_{11}$; $nC_6H_{10}O_5$ (Neubauer, *J. pr.* 62, 193; 71, 255); $C_{12}H_{22}O_{11}$ (Scheibler, *B.* 6, 612); $C_{89}H_{142}O_{74}$ (O'Sullivan, *C. J.* 45, 41).

Occurrence.—It is a constituent of probably all lævorotatory gums, and has been isolated from Levantine, Senari, East Indian, Senegal, and Turkey, gum; these gums contain also, as a rule, other acids different from, but closely allied to arabic acid (O'Sullivan). It exists in sugar-beet (Scheibler), and in the extract of yeast obtained by boiling water (Schützenberger, *Bl.* [2] 21, 204; *C. R.* 78, 493). The beet gum is probably related to arabic acid, but there is no evidence that the yeast-extract body belongs to the arabin group. Many gum-like constituents of seeds and roots are referred to as gums, but the great bulk of them obviously hold no relation to arabic acid. It is found in certain animals (Städeler, *A. Ph.* 111, 26).

Formation.—It is a product of the action of sulphuric acid on algæ-mucilage (Brown, *Ed. Ph. I.* 26, 409); on quince, linseed, and flea-wort mucilages, cellulose being at the same time produced (Kirchner a. Tollens, *A.* 175, 205); and on metagummic acid (Frémy, *C. R.* 50, 125). Cellulose is transformed into gum in plants (Mercadante, *G.* 5, 408). In none of these cases have we any information as to the character of the gum produced.

Preparation.—The lævorotatory gums are principally potassium, magnesium, and calcium salts of arabic or allied acids; they contain from 12 to 18 p.c. water, and yield 2·7 to 3·0 p.c. ash consisting almost wholly of carbonates of these metals. Any one of these gums is dissolved in the least possible quantity of water, the solution is allowed to stand, and, when clear, decanted from any insoluble matter. To the clear liquid twice or thrice as much HCl as is sufficient to convert the bases into chlorides is added, and the gum-acid or acids are precipitated by a moderate excess of alcohol. If the gum contains only arabic acid, the whole pp. can be purified as is described below when dealing with one of the fractions; but if, as is very frequently the case, other allied acids are also present, it is necessary to have recourse to fractional precipitation to isolate the arabic acid. It is found in the fractions least soluble in dilute alcohol, and may be obtained as follows:—The

curdy pp., produced by excess of alcohol in presence of HCl, is well washed with spirit, and then pressed as free from it as possible. It is redissolved in warm water, care being taken to avoid heating for any length of time, because even the small quantity of HCl retained by the pp. has a tendency on heating even for a short time to decompose the arabic acid, as will be described below. The solution is cooled, and alcohol gradually added with continual stirring. In this way, the liquid can be made milky without the formation of a pp.; from this 'milk' the acid or acids can be precipitated in successive fractions by the addition of HCl in carefully graduated quantities. If 4 or 5 fractions are obtained, one or more of them is arabic acid. Each fraction is freed from ash by repeated precipitation from aqueous solution with alcohol in the least possible excess in presence of HCl, and from HCl by repeated precipitation from concentrated solution by the rapid addition of strong alcohol, whereby the production of a 'milk' is obviated. The fractions thus purified are treated with alcohol (S.G. ·81) to render them friable, rubbed down to a powder, filtered out, pressed, and dried over sulphuric acid. Thus prepared they are white, friable bodies, easily soluble in water. If in this state they are exposed for any length of time to a temperature of 100°, they are converted into the meta modifications (meta acids) which are insoluble in water and only swell up to jelly-like masses when treated with it. If, however, they are previously dried *in a vacuum* over sulphuric acid until the weight becomes constant, they can then be dried at 100° without becoming insoluble. The fraction or fractions which are found to have an optical activity, $[\alpha]_j = -26°$ to $-28°$, and which, when again divided, yield fractions each of which has the same activity, consist of arabic acid.

Properties.—Arabic acid, when slowly dried out of syrupy solutions, on glass plates, is a brittle, transparent, colourless, glassy body, soluble in water. During the drying process, especially if a little mineral acid is present, the acid is frequently converted into the meta modification. Solutions of the body are strongly acid to litmus paper, and have a sharp acid taste; they completely neutralise solutions of the alkalis and alkaline earths, and decompose carbonates. The salts of the alkaline earths are precipitated out of solution by alcohol; those of the alkalis are not precipitated under the same conditions, but yield peculiar milky or opalescent solutions from which arabic acid, with some of the alkaline salt, is precipitated on the addition of stronger acids. $BaSO_4$, PbS, and other sulphides, and some hydrates precipitated in solutions of arabic acid, cannot be filtered out, but pass, in greater part, through the filter. Fine animal charcoal is carried through in the same way (C.O'S.). Gum arabic prevents the precipitation of the alkaloids by phosphomolybdic acid, potassium-mercury iodide, and tannin (Lefort a. Thibault, *J. Ph.* [5] 6, 169). These are properties common to all the gum acids. The defining characters of arabic acid are its optical activity, viz. $[\alpha]_j = -26°$ to $-28°$, for solutions containing 5 to 6 grams dry substance in 100 c.c., and the composition of its neutral barium and calcium salts; in the dry state, the former contains 6·0 p.c. BaO and the latter 2·28 p.c. of CaO (O'S.). Solid gum roasted with oxalic acid yields metagummic acid (Frémy), this is dissolved by solutions of the alkalis and alkaline earths with the reproduction of arabic acid (*v.* Rhem. *D. P. J.* 216, 539). Gum arabic and tragacanth are rendered insoluble by potassium bichromate and light (Eder. *J. pr.* 19, 299). Gum, even in small quantities, injected into the blood diminishes the elimination of urine, large doses completely stop the secretion, with a marked increase of blood pressure (Richet a. Montard-Martin, *C. R.* 90, 88).

Reactions.—1. Heated with moderately strong *nitric acid*, arabic acid yields mucic (*v.* Kiliani, *B.* 15, 34), saccharic, oxalic, and tartaric (Liebig) acids; with fuming nitric acid it yields substitution products.—2. Gum heated in sealed tubes with *bromine* yields a colourless or yellowish liquid, probably $C_{12}H_{20}O_{10}Br_4$, which, when treated with silver oxide, lead oxide, or caustic soda, is converted into isodiglycolethylenic acid, $C_{12}H_{20}O_{12}$ (Barth a. Hlasiwetz, *A. Ch. Pharm.* 122, 96). It is possible some of the decomposition products of arabic acid would yield the same results. 3. Gum arabic or arabin when heated to 150° with 2 parts *acetic anhydride* yields tetracetyl-diarabin (?) $C_{12}H_{16}(C_2H_3O)_4O_{10}$; and, when heated to 180° with 6 to 8 parts of the anhydride, a body having the composition $C_{12}H_{15}(C_2H_3O)_5O_{10}$; these acetyl derivatives are white amorphous powders (Schützenberger a. Naudin, *A. Ch.* [4] 21, 235). These bodies are certainly not derived from arabic acid as a whole, but from some one of its decomposition products (C.O'S.).—4. *Pepsin*, in dilute HCl solution, acts on dextrorotatory gum acid, arabinose being amongst the products; *pancreatin* has no action (Fudakowski, *B.* 11, 1072). 5. (*a*) Gum arabic left for some time in contact with *sulphuric acid* is converted into dextrin (!) and, on boiling, yields a sugar probably identical with *galactose* (Berthelot, *C. O.* 21, 219). (*b*) Strong sulphuric acid converts a strong solution of gum in a few hours into metagummic acid; but gum arabic freed from lime by oxalic acid is not transformed in the same way (Frémy). (*c*) Pulverised gum arabic, triturated with strong sulphuric acid, yields sulphogummic acid and a peculiar gum resembling that produced from linen by the action of sulphuric acid (Braconnot) and not capable of fermenting with yeast (Guérin-Varry). (*d*) Arabic acid, digested with dilute sulphuric acid, yields a crystallisable sugar, a non-crystallisable one, and an acid the barium salt of which is insoluble in alcohol: gums from different sources yield these bodies in various proportions, some varieties yielding scarcely any of the crystallisable sugar (Scheibler, *B.* 6, 612). (*e*) A solution containing 30 grams arabic acid (pure), 100 c.c. water, and 2 grams sulphuric acid, yields, on digestion at 100° for 15 minutes, at least two sugars and a new acid the Ba salt of which is insoluble in alcohol: the following equations represent the change:—

$$\text{I. } \underset{\text{arabic acid}}{C_{89}H_{142}O_{74}} + H_2O = \underset{\alpha\text{-arabinosic acid}}{C_{83}H_{132}O_{69}} + \underset{\alpha\text{-arabinose}}{C_6H_{12}O_6}$$

$$\text{II. } C_{83}H_{132}O_{69} + H_2O = \underset{\beta\text{-arabinosic acid}}{C_{77}H_{122}C_{64}} + \underset{\alpha\text{- or }\beta\text{-arabinose}}{C_6H_{12}O_6}$$

$$\text{III. } C_{77}H_{122}O_{64} + H_2O = \underset{\gamma\text{-arabinosic acid}}{C_{71}H_{112}O_{59}} + \underset{\beta\text{-arabinose}}{C_6H_{12}O_6}$$

Continued digestion produces changes that may be represented as follows:—

III. IV. V. VI. VII. and VIII.

$C_{77}H_{122}O_{64} + 9H_2O = C_{41}H_{68}O_{37} + 6C_6H_{12}O_6$
θ-arabinosic acid, β-γ-δ-arabinose.

On further digestion we get:

IX. $C_{41}H_{68}O_{37} + H_2O = C_{35}H_{58}O_{32} + C_6H_{12}O_6$
ι-arabinosic acid δ-arabinose (?)

X. $C_{35}H_{58}O_{32} + H_2O = C_{29}H_{48}O_{27} + C_6H_{12}O_6$
κ-arabinosic acid. δ-arabinose (?)

XI. $C_{29}H_{48}O_{27} + H_2O = C_{23}H_{38}O_{22} + C_6H_{12}O_6$
λ-arabinosic acid δ-arabinose (?)

This last acid is very stable, resisting the action of a boiling 3 to 4 p.c. solution of sulphuric acid for a considerable time (O'Sullivan, *C. J.* 45, 41). α-arabinose is not yet fully described; β-arabinose[1] is Scheibler's arabinose, γ-arabinose is probably identical with galactose, and the remaining sugar or sugars are imperfectly described. These reactions convey some idea of the constitution of the gums of the arabin group, *i.e.* of those which are salts of a gum-acid with alkaline or alkaline-earthy bases, and enable us to understand some of the differences observed in their properties. Those bodies vary considerably in optical activity; this is due (*a*) to the varying proportions of different closely related acids they contain. O'Sullivan found the acid of some samples of gum arabic to consist almost wholly of arabic acid, whilst others contained also α-arabinosic acid, $[\alpha]_j = -36°$, and an acid $(C_{95}H_{152}O_{79})$, $[\alpha]_j = -23°$, with a $C_6H_{10}O_5$ group more than arabic acid. (*b*) To the character and position of the $C_6H_{10}O_5$ group in the acid from the $C_{23}H_{38}O_{22}$ body upwards. Kiliani (*l.c.*) shows that different varieties of gum yield, when oxidised with HNO_3, proportions of mucic acid varying between 14·3 and 38·3 p.c., thus indicating a difference in the number of galactose (γ-arabinose)-yielding groups they contain (see also Scheibler). And (*c*) possibly to the structure of the $C_{23}H_{38}O_{22}$ group itself. The gums, too, vary much in the character of the solutions they yield (Gm. 15, 194); some give a thin syrupy solution, others a thick and jelly-like one; this is due to the varying proportion of the acid naturally converted into the meta modification—the gums which yield the thinnest solutions are those which contain the greatest amount of ash. Gums from the same source have not always the same optical activity; Scheibler found the beet gum of one season +, and of another −; Kiliani states that East Indian gum, and gum arabic elect. are +, the samples of these gums examined by O'Sullivan were −; the sample of Australian gum examined by the former was +, that by the latter, inactive. From this it would appear that the same plant does not produce the same gum in every season, but, on the whole, it is fairly certain that the acids of all the gums are constituted in the same way as arabic acid described above.

Combinations.—The arabic salts of the alkaline earths are prepared by exactly neutralising moderately strong solutions of the pure acid with clear solutions of the earth the salt of which is required, precipitating with alcohol, treating the pp. with strong alcohol until it admits of being powdered, collecting the powder on a filter, pressing, and drying over sulphuric acid. The Ba salt contains $C_{89}H_{142}O_{74}BaO$ (6·0 p.c. BaO) and the CaO salt, $C_{89}H_{142}O_{74}CaO$ (2·28 p.c. CaO). When the syrupy solutions of these salts are allowed to dry spontaneously they yield glassy, transparent masses, like natural gums: the salts of the arabinosic acids yield similar bodies. C. O'S.

[1] According to Kiliani (*B.* 20, 339a, 1233) the formula of arabinose is $C_5H_{10}O_5$; should this prove to be so, the formula of arabic acid and of the arabinosic acids must be diminished by a CH_2O group for every molecule of arabinose-yielding group they contain.

ARABITE $C_5H_{12}O_5$ which is probably $CH_2(OH).CH(OH).CH(OH).CH(OH).CH_2(OH)$. *Penta-oxy-n-pentane.* [102°]. Obtained by reduction of arabinose with sodium-amalgam, keeping the solution carefully neutralised. Small prisms or needles. V. sol. water and hot 90 p.c. alcohol, v. sl. sol. cold alcohol. Sweet taste. Does not reduce Fehling's solution. Does not lose water at 100° (diff. from sorbite) (Kiliani, *B.* 20, 1233).

ARABONIC ACID *v.* TETRA-OXY-VALERIC ACID.

ARACHIC ACID $C_{20}H_{40}O_2$. Mol. w. 312. [75·5°]. *Arachidic acid.*

Occurrence.—1. In the oil from the ground nut *Arachis hypogæa*, from which it is obtained after saponification (Gössmann, *A.* 89, 1).—2. In butter (Heintz, *P.* 90, 146).—3. As glyceryl ether in the fruit of *Nephelium lappaceum* (Oudemans, *J. pr.* 99, 407).

Formation.—1. By potash-fusion from brassidic acid (Goldschmiedt, *J.* 1877, 728).—2. From stearic acid by converting it into the corresponding alcohol, $C_{17}H_{35}CH_2OH$, and iodide $C_{17}H_{35}CH_2I$. The latter gives octadecyl aceto-acetic ether when treated with sodio-aceto-acetic ether, and alcoholic KOH thence produces arachic acid (Schweizer, *Ar. Ph.* [3] 22, 753).

Properties.—Small shining plates; v. sol. boiling alcohol, and ether; insol. water. Gives a nitro-, [70°], and an amido- [59°], arachic acid.

Salts.—(Scheven a. Gössmann, *A.* 97, 257). AgA': prisms (from alcohol)—CuA'$_2$: needles (from alcohol)—BaA'$_2$: hardly soluble in alcohol. – SrA'$_2$– MgA'$_2$: crystalline powder (from alcohol). - KA': usually gelatinous.

Methyl ether. [55°]. Scales (Caldwell, *A.* 101, 97); [53°] (Schweizer).

Ethyl ether. [49·5°]. (296°) at 100 mm.

Iso-amyl ether. [45°]. Scales.

Arachins. Prepared artificially by heating arachic acid with glycerin (Berthelot, *A. Ch.* [3] 47, 355); they are insol. ether. *Di-arachin* $C_3H_5(OH)(OC_{20}H_{39}O)_2$ melts at [75°].

Arachyl chloride $C_{20}H_{39}O.Cl$. [67°]. Unstable (Tassinari, *B.* 11, 2031).

Arachamide $C_{20}H_{39}O.NH_2$. [99°]. Prisms grouped in stars; insol. water, sol. hot alcohol (Gössmann a. Scheven, *A.* 97, 262).

Acetic-arachic anhydride $C_{20}H_{39}O.O.Ac$. [60°]. From AcCl and potassium arachate. Scales (from ether) (T.).

Valeric-arachic anhydride $C_{20}H_{39}O.O.C_5H_9O$ [68°] (T.).

ARALEÏN. The bark of *Aralia spinosa* contains a tannin which gives a green colour with Fe_2Cl_6, and a glucoside called araleïn. The latter is a neutral, light-yellow substance, sol. water and alcohol, insol. ether, benzene, and $CHCl_3$. Gives no pp. with lead acetate, $HgCl_2$, or $PtCl_4$. Boiling dilute HCl converts it into white araliretin, insol. water (Holden, *Ph.* [3] 11, 210).

ARBOL-A-BREA RESIN. The product of a tree (*Canarium album*) growing in the Philippine Islands (Maujean, *J. Ph.* 9, 45; Bonastre, *J. Ph.* 10, 199). Baup (*J. pr.* 55, 83) finds four crystalline substances in it: Amyrin [174°]; Breïdin, S. ·39 at 20°; Breïn [187°]; and Bryoïdin [135°].

ARBUTIN $C_{12}H_{16}O_7$ ½aq. [166°].

Occurrence.—Together with methyl-arbutin in the leaves of the red bearberry, *Arctostaphylos Uva Ursi* (Kawalier, *A.* 82, 241; 84, 356), and in the leaves of a species of winter-green, *Pyrola umbellata* (Zwenger a. Himmelmann, *A.* 129, 203).

Preparation.—The aqueous infusion of the leaves is ppd. by lead acetate, excess of lead removed by H_2S, the filtrate evaporated and the arbutin extracted and crystallised by a mixture of ether (8 pts.) and alcohol (1 pt.). The product is a mixture of arbutin and methyl-arbutin, which can be separated by crystallisation from water (H. Schiff, *G.* 11, 99; 13, 538; *A.* 221, 365; *cf.* Habermann, *M.* 4, 753).

Properties.—Long glistening needles which melt at 165°, but, on second fusion, at 187° (H. Schiff, *B.* 14, 304; *A.* 206, 159). V. sol. alcohol and boiling water, v. sl. sol. ether. Its aqueous solution gives no pp. with lead acetate or subacetate. Does not reduce alkaline cupric solution. Dilute Fe_2Cl_6 gives a blue colour.

Reactions.—1. Split up by emulsin or by boiling dilute H_2SO_4 into hydroquinone and glucose (Strecker, *A.* 107, 229).—2. H_2SO_4 and MnO_2 form quinone.—3. Converted by Ag_2O into water and di-arbutin, an extremely soluble syrup, whence arbutin can be recovered by reduction with Zn and H_2SO_4 (Schiff, *A.* 154, 244).—4. *Chlorine* passed into an aqueous solution forms di-, and tri-chloro-quinones (Strecker, *A.* 118, 295).

Acetyl derivative $C_{12}H_{11}Ac_5O_7$. Plates or needles (from alcohol), insol. water.

Benzoyl derivative $C_{12}H_{11}Bz_5O_7$. Crystalline powder, sl. sol. alcohol.

Di-nitro-arbutin $C_{12}H_{14}(NO_2)_2O_7$. Golden needles (from water); insol. ether (Hlasiwetz, a. Habermann, *A.* 177, 343). Gives an orange pp. with lead subacetate. Boiling dilute H_2SO_4 gives di-nitro-hydroquinone. Converted by Ac_2O into $C_{12}H_9Ac_5(NO_2)_2O_7$.

Methyl-arbutin $C_{13}H_{18}O_7$ *i.e.* $C_6H_7O(OH)_4.O.C_6H_4.OMe$. [169°] (Michael); [175°] (Schiff). Occurs in nature associated with arbutin. Formed synthetically by the action of acetochlorhydrose upon potassium hydroquinone methyl ether, $KO.C_6H_4.OMe$ (Michael, *Am.* 5, 178; *B.* 14, 2097). Also from crude arbutin by converting the free arbutin into methyl-arbutin (by MeI and KOH) or into benzyl-arbutin (H. Schiff, *G.* 12, 464; *A.* 221, 366).

Properties.—Colourless silky needles, with bitter taste. Contain aq and melt at 169° (Michael); contain ½aq and melt at 175° (Schiff). Sol. water and alcohol, v. sl. sol. ether. Gives no blue colour with Fe_2Cl_6.

Benzyl-arbutin $C_{19}H_{22}O_7$ *i.e.* $PhCH_2O.C_6H_4O.C_6H_{11}O_5$ aq. [161°]. S. ·19 at 23°. From $PhCH_2Br$, commercial arbutin (containing methyl-arbutin), and KOH in boiling alcohol. Excess of KOH is removed by CO_2, and after evaporating and adding water, benzyl-arbutin is ppd. while methyl-arbutin remains in solution. Arborescent needles. Soluble in boiling water, very soluble in alcohol. Does not reduce Fehling's solution, except after short boiling with H_2SO_4 which splits it up into glucose and benzyl-hydroquinone. Gives on nitration yellow needles which are benzyl-nitro-arbutin, $C_{19}H_{21}(NO_2)O_7$, [143°], split up by dilute H_2SO_4 into glucose and benzyl-nitro-hydroquinone (Schiff a. Pellizzari, *A.* 221, 365).

Isoamyl-arbutin. From the mixture of arbutin and methyl-arbutin by amyl bromide and NaOH (S. a. P.). Needles. On decomposition gives iso-amyl-hydroquinone and glucose.

ARCHIL or *Orseille* is a purple dye obtained from various lichens (*Roccella, Lecanora,* and *Variolaria*) containing acids (*erythric, lecanoric, &c.*), which on decomposition yield orcin (*q. v.*) which is converted by air and ammonia into red orcein. When K_2CO_3 or Na_2CO_3 as well as ammonia is added to the lichens litmus is produced.

ARGININE $C_6H_{14}N_4O_2$. Easily soluble in water; reacts alkaline. Occurs to the extent of about 3-4 p.c. in the young shoots of the lupine (*lupinus luteus*). The shoots are extracted with water; tannin and lead acetate are added to the extract; the filtrate is acidified with H_2SO_4, again filtered, and ppd. with phosphomolybdic acid; the pp. is washed and treated with cold milk of lime, and the solution of the base finally neutralised with HNO_3 and evaporated to crystallisation.

Salts.—$B'HNO_3$ ½aq: slender white soluble needles; with phosphomolybdic acid it gives a white pp. soluble in hot water; with picric acid a yellow crystalline pp. is formed on standing. — $B'HCl$: large crystals. — $B'_2Cu(NO_3)_2$ 3aq: formed by heating a solution of the nitrate with cupric hydrate; dark-blue prisms, sl. sol. cold water (Schulze a. Steiger, *B.* 19, 1177).

ARGOL. Crude acid potassium tartrate deposited from wine.

ARGYRÆSCIN $C_{27}H_{42}O_{12}$. A glucoside in the cotyledons of the horse-chestnut. Minute tables (from dilute alcohol). Split up by dilute HCl into argyræscetin $C_{21}H_{30}O_6$ and glucose. Potash produces propionic acid and æscinic acid (*q. v.*) (Rochleder, *J. pr.* 87, 1; 101, 415).

ARIBINE $C_{23}H_{20}N_4$. S. 12·9 at 23°. A base extracted by dilute H_2SO_4 from the bark of *Arariba rubra*, the solution being treated with lead acetate and the base dissolved in ether, from which it separates as anhydrous pyramids or (with 8 aq) as four-sided prisms. V. sol. water and alcohol, m. sol. ether (Rieth a. Wöhler, *A.* 120, 247). Salts.—$B''2HCl$.—$B''H_2PtCl_6$.—$B''H_2SO_4$.—$B''2H_2SO_4$.

ARICINE $C_{23}H_{26}N_2O_4$. [188°]. S. (ether) 5 at 18°. '*Cusconine*,' *Cinchovatine*. Yellow Cusco bark contains ·24 p.c. aricine and ·37 p.c. cusconine. Occurs also in bark of cinchona cupræa (Hesse, *Ph.* [3] 12, 517). Prisms (from dilute alcohol); insol. water, v. e. sol. chloroform, m. sol. ether, v. sl. sol. alcohol. Solutions are not fluorescent. Lævorotatory in alcoholic or ethereal solutions; its solution in dilute HCl is inactive. In a 1 p.c. ethereal solution $[\alpha]_D = -94·8°$; in a 1 p.c. alcoholic (97 p.c.) solution $[\alpha]_D = -54°$. Aricine is turned dark green by conc. HNO_3. Bleaching-powder and NH_3 only give a yellowish colour.

Salts. — B'HCl 2aq. — $B'_2H_2PtCl_6$ 6aq. — B HI. — $B'HNO_3$. — $B'_2H_2SO_4$: slender needles, m. sol. cold water.—$B'H_2SO_4$: small prisms, v. sl. sol. cold water.—B'HOAc 3aq: grains, v. sl. sol. cold water.—$B'H_2C_2O_4$ 2aq: white prisms, quickly changing to rhombohedra, S. ·049, sl. sol. hot alcohol. — B'HSCy. — Salicylate $B'C_7H_6O_3$ 2aq.

References.—Pelletier, *A. Ch.* [2] 42, 330; 1, 185; Pelletier a. Corriol, *J. Ph.* [2] 15, 575; Severkōhn, *Repert. f. Pharm.* 33, 357; Manzini, *Ph.* [3] 2, 95; Howard, *Ph.* [3] 5, 908; Hesse, *A.* 166, 259; 181, 58; 185, 321; 200, 303.

ARNICIN $C_{20}H_{30}O_4$ (?). An amorphous substance present in the root, leaves, and blossoms of *Arnica montana* (Walz, *N. Jahrb. Pharm.* 3, 175; 14, 79; 15, 329).

AROMATIC SERIES. Substances whose molecules contain a benzene nucleus are said to belong to the aromatic series.

Elements attached to a carbon atom belonging to the benzene nucleus are more firmly fixed than when attached to a carbon atom not in that nucleus: in the former case the derivative (called an *eso* derivative) has the character of a derivative of benzene, in the latter case the derivative (called an *exo* derivative) behaves like a fatty compound. Thus *exo*-chloro-toluene (benzyl chloride) $C_6H_5CH_2Cl$ behaves like ethyl chloride, being readily converted into an alcohol, amine, or cyanide, by treatment with KOH, NH_3, or KCN, respectively; while *eso*-chloro-toluene, $C_6H_4Cl.CH_3$, is not affected by these reagents.

It must, however, be added that the ease with which a given atom or radicle in the molecule of an aromatic compound may be displaced depends not only upon its position in relation to the carbon atoms but also upon the existence and position of other elements or radicles in the molecule. Thus *o*- and *p*-, but not *m*-, chloro-nitro-benzene are converted by hot aqueous potash into nitro-phenols, and by NH_3 into nitro-anilines; while chloro-phenols and chloro-benzene sulphonic acids are converted into di-oxy-benzenes by potash-fusion.

Halogens acting upon cold hydrocarbons in the presence of carriers (such as I) enter the benzene nucleus, but when acting alone upon hydrocarbons at 100° or upwards they enter a side chain (*exo* position). Direct sunlight has the same effect as elevation of temperature, but its effect is entirely counteracted by the presence of iodine (Schramm, *B.* 18, 606). Halogens attack a benzene nucleus that already contains hydroxyl, amidogen, or SO_3H, with much greater vigour than when its carbon atoms are united only to hydrogen and carbon.

Conc. HNO_3 and conc. H_2SO_4 attack aromatic compounds, NO_2 and SO_3H displacing H in the nucleus; they do not act upon fatty compounds in this way.

The constitution of the molecule of benzene, and the methods by which the relative position of elements or radicles in the molecules of its derivatives have been determined will be discussed in another article, *v.* BENZENE.

Laws of Substitution.—I. When one of the following radicles has displaced one of the atoms of hydrogen in the benzene molecule, forming the compound C_6H_5A, any new group on entering will take up a position *meta* to A. Here A may be CO_2H, SO_3H, or NO_2, and probably also CN, CHO, SO_2Ph, and $CO.CH_3$ (Hubner, *B.* 8, 873; Nölting, *B.* 9, 1797; *cf.* Armstrong, *C. J.* 51, 259; Morley, *C. J.* 51, 579).

II. If in a substituted benzene, C_6H_5B, the substituting element or radicle be not one of the [illegible]ing, then any new group on entering will take up an *ortho* or a *para* position: usually chiefly *p* with a little *o*. Examples of B are NH_2, NHAc, OH, Cl, Br, I, CH_3 and all chains of carbon atoms except such as begin with CO.

These laws tell the chief product of the substitution [illegible] of isomerides at variance wit[illegible] be formed.

The radicles [illegible] meta substitution are all composed of an element (N, C, or S) united to a chlorous group; CCl_3 is also a radicle of this kind, and it gives a *m*-nitro-derivative, but it also gives a *p*-chloro-derivative.

The radicles that induce *p* or *o* substitution are either single elements, or elements united to basylous elements or groups. The radicles CH_2Cl and $CHCl_2$ are intermediate in character; the latter appearing to resemble CCl_3, the former resembling CH_3. Armstrong points out that the radicles producing *m* derivatives are unsaturated, and might form additive compounds before substitution takes place.

Amido compounds in presence of excess of H_2SO_4 (20 pts.) when treated with the calculated quantity of HNO_3 dissolved in H_2SO_4, added at 0°, give chiefly meta-nitro derivatives, some of the *p*-nitro derivative being also formed. Examples: aniline, acetanilide, toluidine, xylidine, *p*-bromo-aniline (Nölting a. Collin, *B.* 17, 261), di-methyl-aniline, di-ethyl-aniline (Groll, *B.* 19, 198), ethyl-aniline (Nölting a. Strecker, *B.* 19, 546). The amount of meta-nitro derivative formed is increased by increasing the quantity of sulphuric acid present. In all these cases nitrogen is attached to a chlorous radicle, aniline sulphate being $C_6H_5N(O.SO_3H)H_3$, and might therefore be expected to produce a meta derivative. It is, however, curious that a solution of aniline sulphate in a small quantity of sulphuric acid gives very little *m*-nitraniline on nitration.

When a new element or radicle enters a benzene nucleus in which more than one H is already displaced if it can satisfy the requirements of each of the substituents already present it will do so; if not it obeys the most powerful substituent present. The following appears to be the order of priority, beginning with the strongest:

HO; NH_2; halogens; CH_3; other alkyls; NO_2; CO_2H and SO_3H. The conversion of *p*-nitro-phenol into $C_6H_3(OH)Br(NO_2)$ [1:2:4], and that of *o*-nitro-phenol into $C_6H_3(OH)Br(NO_2)$ [1:5:2], by the action of Br are instances where both NO_2 and OH are obeyed; but in the action of Br upon *p*-bromo-phenol and of HNO_3 upon $C_6H_3(OH)Cl_2$ [1:2:4] the new substituent obeys the stronger radicle, producing $C_6H_2(OH)Br_3$ [1:2:4:6] and $C_6H_2(OH)Cl_2(NO_2)$ [1:2:4:6] respectively.

When a hydrocarbon radicle is introduced by the agency of $AlCl_3$ it does not always follow the foregoing rule; thus *m*-xylene is the chief product of the action of MeCl upon benzene in presence of $AlCl_3$.

Differences between o, m, and p compounds. Ortho, meta, and para compounds usually boil at about the same temperature, but the para compounds have the highest melting-points. The ortho compounds are usually the most, and the para compounds the least, volatile with steam. In the oxidation of ortho compounds the benzene ring is liable to be broken up, while in the meta and para compounds this is not the case (v. HYDROCARBONS). Ortho compounds readily give rise to products of condensation in which the side chains may be supposed to be joined in the form of a ring; this tendency is observed to some extent in the para series but not at all in the meta series. Thus by loss of H_2O *o*-amido-phenyl-glyoxylic acid gives isatin; *o*-amido-cinnamic acid gives carbostyril, *o*-oxy-cinnamic acid gives coumarin; phthalic acid gives phthalic anhydride.

o-nitraniline hydrochloride is readily decomposed by water, *p*-nitraniline hydrochloride less so, and *m*-nitraniline hydrochloride is hardly decomposed by water (Lellmann, *B.* 17, 2719). In general, the introduction of a radicle into the *m*-position produces less change in the properties of a compound than the introduction of the same radicle into the *o* and *p* position, and of the resulting derivatives the meta are the most stable. Thus *m*-xylene is oxidised with difficulty, while dilute HNO_3 readily converts *o*-, and *p*-, xylene into toluic acids. Ortho-, and para-, oxybenzoic acids are converted into phenol by heating with aqueous HCl in sealed tubes, while *m*-oxybenzoic acid, like benzoic acid itself, is unaffected. Ammonia converts *o*- and *p*- nitro-anisols into nitranilines, but does not affect *m*-nitro-anisol or anisol itself; similarly ammonia converts *o*-, and *p*-, bromo-nitro-benzenes into nitranilines, but does not affect *m*-bromo-nitro-benzene or bromo-benzene itself. Boiling alkalis convert *o*-, and *p*-, nitraniline into nitrophenols, but do not affect *m*-nitraniline or aniline. Aniline and *m*-nitraniline resemble one another in readily uniting with phenyl thio-carbimide (forming diphenyl-thio-urea and nitro-di-phenyl-thio-urea respectively), while *p*-, and *o*-, nitraniline require to be heated for some time with phenyl thio-carbimide before they will combine. Benzoic acid and *m*-oxy-benzoic acid are readily reduced by sodium-amalgam to benzyl alcohol and *m*-oxy-benzyl alcohol respectively, while *o*-, and *p*-, oxybenzoic acids are not attacked. Ortho- and para-nitro-acetanilide dissolve in conc. potash; the former is readily saponified by the potash, giving potassium acetate and *o*-nitro-aniline; a similar decomposition occurs with the latter, but with greater difficulty. Meta-nitro-acetanilide is insoluble in conc. potash, and is scarcely affected by it (Kleemann, *B.* 19, 336). The substitution of an atom of hydrogen in the nucleus by an atom of bromine is accompanied by absorption of heat; in an actual experiment this is not observed, being more than counterbalanced by the heat developed in the simultaneous formation of HBr (Werner, *Bl.* 46, 282).

Occasional reactions.

1. *Acetyl bromide* not only displaces H by Ac but sometimes even turns out an alkyl; thus it converts di-methyl-aniline and di-ethyl-aniline into methyl acetanilide, and ethyl-acetanilide respectively (Staedel, *B.* 19, 1947).—2. *Benzoyl chloride* sometimes behaves in the same way, converting di-methyl-aniline and di-ethyl-aniline into methyl-benzanilide and ethyl-benzanilide respectively.—3. *Nitric acid* in nitration sometimes turns out acetyl, converting ethyl acetanilide into $C_6H_3(NO_2)_2NEtH$ [1:3:4], and behaving similarly towards methyl acetanilide (Norton, *B.* 18, 1997). Nitric acid sometimes turns out bromine; thus it converts *p*-bromo-aniline into tri-nitro-aniline (picramide) (Hager, *B.* 18, 2578).—4. *Potash* converts di-nitro-di-methyl-aniline, $C_6H_3(NO_2)_2NMe_2$ [4:2:1] into di-nitro-phenol, di-methyl-amine being given off.

Molecular changes.

At high temperatures *o*-compounds may change to *p*-, and both *o*- and *p*- to *m*-. At 100° *o*-phenol-sulphonic acid changes to *p*-phenol-sulphonic acid. At 220° potassium salicylate changes to *p*-oxybenzoate, while sodium salicylate is not affected at that temperature. Resorcin is obtained by potash-fusion from benzene *p*-disulphonic acid, *p*-chloro-benzene sulphonic acid, and *o*- and *p*-bromo-phenol.

Methyl can pass from combination with nitrogen into the nucleus; thus dimethylaniline methylo-iodide at 220° gives *o*- and *p*- dimethyl toluidine, methyl-xylidine, and di-methyl-xylidine; while at 335° it gives ψ-cumidine, $C_6H_2Me_3NH_2$ (Hofmann, *Pr.* 21, 47).

Ethyl aniline hydrochloride at 320° changes similarly to ethyl-phenyl-amine, $C_6H_4EtNH_2$, while isoamyl-aniline hydrochloride becomes isoamyl-phenyl-amine, $C_6H_4(C_5H_{11})NH_2$ (Hofmann, *B.* 7, 526). In these cases it may be supposed that MeI, MeCl, EtCl, and $C_5H_{11}Cl$ respectively are split off and then attack the nucleus; this action of MeCl is seen in the conversion of xylidine hydrochloride into ψ-cumidine by heating with methyl alcohol at 280° (Hofmann, *B.* 13, 1730).

Conversion of fatty compounds into aromatic.

1. By passing acetylene (*q. v.*) through a red hot tube.—2. By heating acetone or allylene with sulphuric acid mesitylene is formed.—3. Uvitic acid, $C_6H_3Me(CO_2H)_2$ [1:3:5] is formed by boiling pyruvic acid with baryta.—4. Oxy-uvitic ether is formed by the action of chloroform on sodium aceto-acetic ether.—5. Succinylo-succinic ether from succinyl chloride, sodium, and succinic ether is di-oxy-di-hydro-terephthalic ether; when heated with KOH it gives hydroquinone. Hydroquinone is also formed when succinates are subjected to dry distillation.—6. Phloroglucin tri-carboxylic ether is formed by the action of sodium or of $ZnEt_2$ on malonic ether (Baeyer, *B.* 18, 3457; Lang, *B.* 19, 2937). 7. Tri-mesic ether is formed by the action of sodium on a mixture of formic and acetic ether (Piutti, *B.* 20, 537).—8. Hexyl iodide and bromine at 200° gives hexa-bromo-benzene (Krafft, *B.* 9, 1085; 10, 801).—9. K and CO combine, forming $C_6(OK)_6$ (Nietzki a. Benckiser, *B.* 18, 1833).

Conversion of aromatic compounds into fatty.

1. Carbonic, oxalic, and formic acids are products of oxidation of aromatic compounds.—

2. Benzene is converted by $KClO_3$ and HCl into $C_3H_2Cl_2O_3$, which is converted by baryta into fumaric acid.—3. Nitrous acid converts pyrocatechin in ethereal solution into dioxytartaric acid.—4. HCl and $KClO_3$ convert gallic acid into tri-chloro-glyceric acid.—5. Chlorine passed into a cold aqueous solution of phloroglucin gives dichloro-acetic acid (Hlasiwetz a. Habermann, *A.* 155, 132).

Aromatic acids. The principal aromatic acids are those containing SO_3H and those containing CO_2H. The former will be discussed as SULPHONIC ACIDS, the latter will be briefly characterised here (*v.* also ACIDS, AMIDO-, BROMO-, CHLORO-, IODO-, and NITRO-acids).

Formation.—1. By oxidation of homologues of benzene or derivatives of such homologues. $K_2Cr_2O_7$ (2 pts.), H_2SO_4 (3 pts.), and water (3 to 5 pts.), is a convenient mixture for the purpose; but it converts all side chains into carboxyls, thus *m*- and *p*- xylene become iso-, and tere-, phthalic acids, while mesitylene becomes trimesic acid. Dilute HNO_3 (S.G. 1·2) and aqueous $KMnO_4$ oxidise more gradually, attacking one side chain at a time, thus converting *o*- and *p*-xylene into *o*- and *p*- toluic acid and mesitylene into mesitylenic acid.—2. By passing CO_2 over a mixture of a bromo-derivative and sodium: $C_6H_5Br + CO_2 + Na_2 = C_6H_5CO_2Na + NaBr$ (Kekulé, *A.* 137, 178).—3. By heating a bromo-derivative with chloroformic ether and sodium, thus: $C_6H_5Br + ClCO_2Et + Na_2 = C_6H_5CO_2Et + NaCl + NaBr$ (Wurtz, *A. Suppl.* 7, 125).—4. By the action of $COCl_2$ or CO_2 on aromatic hydrocarbons in presence of $AlCl_3$ (Friedel a. Crafts, *v.* ALUMINIUM CHLORIDE, p. 147) the product being treated with water. The amides may be produced in a similar way by using $Cl.CO.NH_2$ instead of $COCl_2$ (Gattermann a. Schmidt, *B.* 20, 58).—5. By heating sulphonates with sodium formate: $PhSO_3K + HCO_2Na = Ph.CO_2Na + HSO_3K$ (V. Meyer, *A.* 156, 273).—6. By saponification of nitriles. The nitriles may be obtained either by heating sulphonates or *exo*-chloro derivatives with potassium cyanide or by heating thio-carbimides with copper (Weith, *B.* 6, 212). Nitriles may also be obtained by distilling the formyl derivatives of amines with zinc-dust, *e.g.*: $PhNH.CHO = H_2O + PhCN$.—7. By oxidation of alcohols or aldehydes.—8. Aromatic acids containing carboxyl in the side chain can be prepared by synthesis with aid of aceto-acetic ether (*q.v.*) or of malonic ether (*q. v.*).—9. Oxy-acids are formed by boiling diazo-acids with water, or by potash-fusion from chloro-, bromo-, iodo-, or sulpho-, acids.—10. By passing CO_2 into sodium phenols at 180° or potassium phenol; in the former case CO_2H takes up a position ortho to the hydroxyl. Potassium phenol at 140° gives salicylic acid, but at 170°-200° it gives *p*-oxy-benzoic acid. The reaction takes place in two stages:

$$C_6H_5.O.Na + CO_2 = C_6H_5.O.CO_2Na;$$
$$C_6H_5.O.CO_2Na = C_6H_4(OH).CO_2Na$$

(*v.* OXY-BENZOIC ACIDS).—11. By heating phenols with dilute alcoholic solution of CCl_4 and NaOH at 100°: $C_6H_5OH + CCl_4 + 6NaOH = C_6H_4(ONa)CO_2Na + 4NaCl + 4H_2O$ (Tiemann a. Reimer, *B.* 9, 1285). The carboxyl takes up positions para and ortho to the hydroxyl.—12. Perkin's synthesis of cinnamic acid and its homologues is described and discussed in the article on ALDEHYDES.—13. Resorcin and its homologues are converted into (1, 3, 4) and (1, 3, 2) di-oxy-benzoic acids and their homologues by heating with ammonium carbonate and water; while hydroquinone and its homologues heated with potassium bicarbonate, water, and a little K_2SO_3 give (1, 4, 2) di-oxy-benzoic acid and its homologues (Senhofer, *Sitz. B.* 80, 504; 81, 430, 1044; *M.* 2, 448).

Reactions.—1. The aromatic acids are subject to the general laws governing substitution in the benzene nucleus.—2. They are usually sl. sol. water but v. sol. alcohol and ether. The homologues of benzoic, and of salicylic, acid are volatile with steam, *m*-, and *p*-, oxy-benzoic acids are not volatile with steam. Salicylic acid and its homologues are soluble in chloroform, *p*-oxy-benzoic acid and its homologues are not. Ortho-oxy-acids are also characterised by giving a violet colouration with Fe_2Cl_6.—3. Ortho-oxy-acids of the form $C_6H_4(OH).CH_2.CO_2H$ or $C_6H_4(OH).CH_2.CH_2.CO_2H$ have a tendency to produce anhydrides or lactones; ortho-amido acids of the form $C_6H_4(NH_2).CH_2.CO_2H$ or $C_6H_4(NH_2).CH_2.CH_2.CO_2H$ readily form anhydrides, similarly called lactams: $C_6H_4{<}{\scriptstyle CH_2 \atop \scriptstyle NH}{>}CO$, or lactims: $C_6H_4{<}{\scriptstyle CH_2 \atop \scriptstyle N}{\geqslant}C.OH$.—4. Benzene is produced by fusion with NaOH from benzoic acid (75 p.c.), trimellitic acid, hydrocinnamic acid, and cinnamic acid (50 p.c.); a little diphenyl is also formed. Fusion with NaOH converts *o*-, and *p*-, oxy-benzoic acids into phenol (50 to 60 p.c.); protocatechuic acid into resorcin (50 to 60 p.c.); (1,3,5)-di-oxy-benzoic acid into resorcin (60 p.c.), phloretic acid and *p*-coumaric acid into *p*-oxy-benzoic acid and finally into phenol; oxy-terephthalic acid into salicylic and *p*-oxy-benzoic acids, and finally into phenol (Barth a. Schreder, *B.* 12, 1255).

Aromatic bases. The preparation and properties of the aromatic bases have been discussed in the article on AMINES. They may be divided into two classes according as the nitrogen is attached to carbon in a benzene nucleus or in a side chain; bases of the latter form resemble fatty amines. Amines containing amidogen attached to the benzene nucleus are weakened in basic power by introduction of nitroxyl or halogens into the nucleus, more especially if these radicles do not occupy a position meta to the amidogen. Trichloraniline, dinitraniline, and trinitraniline do not combine with acids; the latter is even saponified by potash with formation of trinitrophenol.

ARSENATES. Salts of arsenic acid, *v.* ARSENIC, ACIDS OF, p. 305.

ARSENIC. As (*Arsenicum, Regulus arsenici,* ἀρσενικόν. By the term σανδαράκη Aristotle seems to mean a compound of arsenic and sulphur, called ἀῤῥενικόν by Theophrastus). At. w. 74·9. Mol. w. 299·6; 149·8 at c. 1700° (Biltz a. Meyer, *B.* 22, 725). Melts only under great pressure (Landolt; also Mallet, *C. N.* 26, 97). S.G. 5·23 to 5·76: pure, crystalline $\frac{14°}{14}$ 5·726–5·728; grey, pearly crystals $\frac{14°}{14}$ 4·71 (Bettendorff, *A.*

144. 110); amorphous $\frac{14^{\circ}}{14}$ 4·710–4·716 (*ibid. l.c.*); fused $\frac{19^{\circ}}{19}$ 5·709 (Mallet, *C. N.* 26, 97). V.D. 147·2 at 860° (Deville a. Troost, *C. R.* 56, 871); 153·7 at 640–670° (Mitscherlich, *A.* 12, 159). S.H. crystallised, ·083; black, amorphous, ·0758 (Bettendorff a. Wüllner, *P.* 133, 293). C.E. (linear at 40°) ·00000559 (Fizeaux, *C. R.* 68, 1125). E.C. (Hg at 0° = 1) 2·679 at 0°, 1·873 at 100° (Matthiessen a. Bose, *T.* 152, 1). S.V.S. cryst. 13·1; amorph. 15·9. $\frac{\mu_A - 1}{d} \times$ at. wt. 15·4 (Gladstone, *Pr.* 18, 49). Chief lines in emission spectrum, *v.* Huntington, *P. Am. A.* [2] 9, 34; Hartley a. Adeney, *T* 1884. 121.

Occurrence.—Found native, but more frequently associated with other metals and sulphur, in widely distributed ores. Obtained as a principal product chiefly from *native arsenic*, *arsenical iron* $FeAs_2$ and Fe_4As_3, and *arsenical pyrites* $FeAsFeS_2$; obtained as a secondary product from *smaltine*, *cobalt glance*, *arsenical cobalt*, *nickel glance*, many *fahl-ores*, &c. Occurs also in ferruginous deposits of certain mineral waters (Will, *A.* 61, 192); in nearly all iron ores (Walchner, *A.* 61, 205); in soils, from the weathering of iron pyrites (Sonnenschein, *Ar. Ph.* [2] 143, 215); in the residue obtained by evaporating sea water (Daubrée, *Ann. M.* [4] 19, 669); frequently found in metallic bismuth (Schneider, *J. pr.* [2] 20, 418); in various kinds of pyrites, and hence in most samples of commercial sulphuric acid, and in many substances in the manufacture of which this acid is used (*v.* H. A. Smith, *P. M.* [4] 44, 370).

Preparation.—On the large scale by heating to redness, out of contact with air, arsenical iron or arsenical pyrites; arsenic sublimes; iron, or ferrous sulphide, remains. Prepared in small quantities at a time by heating As_4O_6 with powdered charcoal, or with 'black flux,' in crucibles covered with conical iron caps. Also by heating As_2S_3 with charcoal, an alkaline carbonate, and KCN. Purified by resublimation after mixing with powdered charcoal; or by heating with a little I (Ludwig, *Ar. Ph.* [2] 97, 23); or by boiling with moderately conc. K_2CrO_4Aq acidified with H_2SO_4 (Böttger, *J. pr.* [2] 2, 131). Arsenic was first prepared from arsenious acid in 1694 by Schröder; its chemical nature was further investigated by Brand (1733), Macquer (1746), Monnet (1773), and others. Scheele discovered arsenic acid and arsenuretted hydrogen in 1775.

Properties.—Very brittle, steel grey, lustrous; crystallises by sublimation in hexagonal rhombohedra isomorphous with Sb and Te; $a:c = 1:1{\cdot}4025$. H = 3·5. When As is sublimed in a rapid H stream in a glass tube the sublimate nearest the heated part of the tube consists chiefly of rhombohedra, that farther from the hottest part but still on a warm portion of the tube (210°–220°) of black amorphous As, while the coolest part of the tube is filled with yellow fumes which condense to grey crystals (Bettendorff, *A.* 144, 110). Black amorphous As is also obtained by condensing As vapour at a fairly high temperature; by decomposing As compounds by heating in glass tubes to moderately high temperatures (*e.g.* AsH_3), or by heating with reducing agents (*e.g.* As_4O_6 with C); or by reduction of As compounds in the wet way (Engel, *C. R.* 96, 497). As can be obtained in regular octahedra by heating a mixture of much H with a little AsH_3 (Cooke, *Am. S.* [2] 31, 91). Amorphous As is changed to crystalline by heating for some time at 310° (Engel, *C. R.* 96, 1314); by heating to 358°–360° (Bettendorff, *A.* 144, 110). Amorphous As when subjected to a pressure of 6500 atmospheres acquires metallic lustre and its S.G. increases (Spring, *B.* 16, 326). The vapour of As is citron-yellow (Le Roux, *C. R.* 51, 171). The spectrum of As shows lines in the orange (6169·5), yellow, and green (5331) (Thalen, *A. Ch.* [4] 18, 244); also many more refrangible lines (*v.* Hartley, *T.* 1884. 124). As combines with Cl and O with production of heat; $[As, Cl^3] = 71{,}390$; $[As^2, O^3] = 154{,}670$; $[As^2, O^3, Aq] = 147{,}120$; $[As^2, O^5] = 219{,}380$; $[As^2, O^5, Aq] = 225{,}380$ (Thomsen). As volatilises at a dark red heat without previous fusion at ordinary pressures. The molecule of As is tetratomic (As_4); the atom is trivalent in gaseous molecules (AsH_3, $AsCl_3$, &c.). The atomic weight has been determined (1) by analysing, and determining V.D. of, various gaseous compounds, AsH_3, $AsCl_3$, AsI_3, As_4O_6, &c.; (2) by determining S.H. of As; (3) by comparing isomorphous compounds of As, Sb, and Bi, arsenates with phosphates and vanadates, &c. (Wallace, *P. M.* [4] 18, 279; Dumas, *A. Ch.* [3] 55, 174; Kessler, *P.* 95, 204).

As is insoluble in alcohol and ether, but is said to be dissolved by certain oils. It oxidises fairly rapidly in air at ordinary temperatures; heated in air, it burns to As_4O_6 with a bluish flame; is oxidised by nitric and sulphuric acids, and by fusion with alkalis. As forms two series of compounds, of which As_4O_6 and As_2O_5 are representatives.

In many of its physical properties As is metallic, but in its chemical relations it is decidedly non-metallic or negative. Exhibits allotropy; oxides are acid-forming (*v.* ARSENIC, OXIDES OF; also ARSENIC, ACIDS OF); at the same time As_4O_6 appears to react with SO_3 to form a salt, and with $KH.C_4H_4O_6$ to form a compound analogous with tartar emetic, and with conc. HClAq to form $AsCl_3$ (*v.* ARSENIOUS OXIDE, under ARSENIC, OXIDES OF). Arsenious acid is unknown, and an aqueous solution of the oxide behaves towards alkalis as a very feeble salt-forming compound; but arsenic acid is as strong an acid as phosphoric, their relative affinities are nearly equal (*v.* AFFINITY, p. 67). The haloid compounds of As do not show any marked tendencies to form double salts. The hydride AsH_3 does not combine with acids, as NH_3 and PH_3 do; but at the same time compounds belonging to the form AsR_4X, where R is an alcoholic radicle C_nH_{2n+1}, and X is a halogen or even OH, are known (*v.* ARSENIC COMPOUNDS, ORGANIC). For a fuller discussion of the chemical relations of arsenic *v.* arts. BISMUTH, CHEMICAL RELATIONS OF; and NITROGEN GROUP OF ELEMENTS.

Reactions.—1. *Hydrochloric acid*, no action in absence of air; in presence of air a little $AsCl_3$ is formed.—2. *Nitric acid* and *aqua regia* react with production of much heat; oxides of N,

As_4O_6, and H_3AsO_4, are formed.—3. Hot. conc. *sulphuric acid* evolves SO_2 and forms As_4O_6.—4. *Molten potash* or *soda* produces an arsenite and H.—5. *Molten nitre* or *potassium chlorate* produces potassium arsenate; the action is more or less explosive.—6. *Solution of sulphur dioxide* reacts, when heated with As in a closed tube to 200°, to produce As_4O_6, S, and H_2SO_4Aq, but no sulphide of As (Geittner, *J.* 1861. 143).—7. *Ammonia solution* is without action on As.

Combinations.—1. With *nascent hydrogen* AsH_3 and AsH are formed (*q. v.*).—2. With *chlorine*, *bromine*, or *iodine*, $AsCl_3$, $AsBr_3$, or AsI_3 (*q. v.*) is produced.—3. With *fluorine* (action of HF on As_4O_6) AsF_3 is formed (*q. v.*).—4. With *oxygen* As combines to form As_4O_6 (*q. v.*); As_2O_5 (*q. v.*) is produced by heating one of its hydrates.—5. The sulphides As_2S_2 and As_2S_3 and As_2S_5 (*q. v.*) are produced by heating together arsenic and *sulphur*; the sulphide As_2S_5 is, however, best obtained by decomposing solutions of alkaline sulpharsenates by acid.—6. *Tellurium* combines with arsenic to form As_2Te_2 and As_2Te_3, when the two elements are melted together in the required proportions (Oppenheim, *J. pr.* 71, 266).—7. When arsenic is melted with *sulphur and selenion* in the proportions represented by the formulæ As_2SeS_2 and As_2SSe_2, two bodies having the compositions indicated are obtained. The first is a lustrous red semi-transparent mass from which the whole of the Se separates out after some days. This body is easily soluble (when powdered) in NH_4HSAq. The body As_2SSe_2 is a crystalline opaque solid which may be distilled unchanged; it is less easily soluble in NH_4HSAq than As_2SeS_2 (v. Gerichten, *B.* 7, 29).—8. Arsenic appears to be incapable of combining with *phosphorus* directly [older experiments by Landgrebe (*S.* 60, 184) probably yielded only a mixture of P and As]; but if AsH_3 is led into PCl_3, or PH_3 into $AsCl_3$, a red-brown solid is obtained (after drying it appears as a darker powder without lustre) which is insoluble in alcohol, ether, and $CHCl_3$, but fairly soluble in CS_2. This solid is PAs; it is changed by water into $P_2As_2O_2$ with which chlorine reacts to produce $AsCl_3$ and $POCl_3$. The compound PAs is rapidly oxidised by concentrated HNO_3, less rapidly by dilute HNO_3, giving H_3AsO_4 and H_3PO_4; solutions of KOH, NH_4OH, or $Ba(OH)_2$, easily decompose PAs rapidly when warm) producing PH_3, AsH_3, H_3PO_2, H_3AsO_3, and As. Heated in air PAs burns to As_2O_3 and P_2O_3; heated in absence of air, or in CO_2, phosphorus sublimes and then arsenic. The reactions of $P_2As_2O_2$ are very similar to those of PAs (*v.* Janowsky, *B.* 6, 216; 8, 1636).—. Arsenic forms *alloys* with many *metals*. Some of these are produced by very strongly compressing the constituents (Spring, *B.* 16, 324). These alloys are generally brittle, they are only partially, in many cases not at all, separated into their constituents by the action of heat out of contact with air; they are generally oxidised to arsenates, and oxides of the metals, by fusion with nitre; fused with alkaline carbonates and sulphur, thio-arsenite or thio-arsenate of the alkali metal is generally produced, and the metals formerly alloyed with the arsenic are completely separated as sulphides. Arsenides of heavy metals are scarcely if at all attacked by nitric acid or aqua regia. Many alloys of arsenic are definite compounds; several of them occur native as minerals (*v.* Winkler, *J. pr.* 91, 193; Sénarmont, *A. Ch.* 80, 221; Rammelsberg, *P.* 128, 441). The alloys with *cobalt*, which are brittle and iron-grey in colour, are formed, with production of heat, by melting the elements together. CoAs occurs native as *Smaltine*; it always contains more or less iron and nickel replacing part of the arsenic. Co_2As_3, generally containing more or less iron, also occurs native as *Skutterudite*, or *Modumite*. Arsenic alloys with *copper* to form white solids which tarnish in the air. According to Lippert (*J. pr.* 81, 168) the grey deposit obtained by heating copper in an HCl solution of arsenious oxide is Cu_5As_2; when this body is heated in hydrogen Cu_6As remains. The compounds Cu_3As, Cu_6As, and Cu_9As, occur native as *Domeykite*, *Algodonite*, and *Darwinite*, respectively. The alloys of arsenic and *iron* are brittle solids formed by melting the elements together; $FeAs_2$ and Fe_4As_3 occur native as *Arsenical iron*, sometimes containing Ag, Au, and Cu. Arsenic alloys with *lead* to form brittle solids. With *nickel*, arsenic alloys easily; Ni_2As is obtained by melting the elements together. The minerals *Copper-nickel* NiAs, and *Cloanthite* $NiAs_2$, occur native; they contain varying quantities of Sb, Fe, Pb, Co, and Cu. A lustrous crystalline alloy Ni_3As_2 is obtained by reducing arsenate of nickel by charcoal at a high temperature; Ni_3As is said to be formed when KCN, As, and NiO are fused together (Descamps, *C. R.* 86, 1065). Arsenic also alloys, with production of much heat, with *potassium* and *sodium*; the products are decomposed by water with formation of KOH (or NaOH)Aq, AsH_3, and As. An alloy of 15 parts *tin* and 1 part arsenic forms large leaf-like crystals. Arsenic is not much used in technical chemistry; the alloy with lead is employed in making shot. Arsenic appears to form alloys with several other metals, especially Hg (?) Pd and Pt. By strongly compressing (6500 atmos.) As with various metals, Spring (*B.* 16, 326) obtained several well-defined alloys, *e.g.* Zn_3As_2, Cu_3As_2, &c. &c.

Detection.—In dry way. Arsenic heated with slight access of air volatilises with a garlic-like odour (probably due to a little As_4O_6) and condenses on cooling as a lustrous black deposit, which is easily converted into a white crystalline sublimate (As_4O_6) by heating in presence of plenty of air. Sulphides or oxides of arsenic, and the salts of arsenious and arsenic acid, yield sublimates of black amorphous arsenic when heated with an alkaline carbonate alone or mixed with charcoal or KCN (*v.* Fresenius, *A.* 49, 301; Rose, *P.* 90, 193). Oxide of arsenic heated with much $NaC_2H_3O_2$ in a tube closed at one end yields cacodyl oxide, recognised by its foul smell.

In wet way. I. *Arsenious compounds.* (i.) *Sulphuretted hydrogen* passed into a solution of As_4O_6, or an arsenite, acidified with HCl, forms a bright yellow pp. of As_2S_3, soluble in NH_4OH, NH_4SH, and $(NH_4)_2CO_3$, solutions, and reprecipitated by HCl. As_2S_3 is said to be soluble in a considerable quantity of boiling water and in boiling dilute HCl (Odling, *Guy's Hosp. Rep.* [3] 1, 239). (ii.) *Neutral solution of silver nitrate* produces a canary-yellow pp. of Ag_3AsO_3 easily soluble in most acids and in

ammonia. (iii.) ***Neutral solution of copper sulphate*** **precipitates green** $CuHAsO_3$ **(Scheele's green) easily soluble in acids and in ammonia.** (iv.) *Reinsch's test* (*J. pr.* 24, 244). A warm solution of an arsenious compound acidified with HCl deposits a film of arsenic on a piece of bright *copper* kept in contact with it for some time; this deposit may be oxidised to As_4O_6 by heating in air (*v. supra*). The deposit consists of. As_2Cu_5 according to Lippert (*J. pr.* 81, 168). Arsenic compounds may be detected by Reinsch's test, if present in considerable quantity (Werther, *J. pr.* 82, 286), even in small quantity if heated for some time with HCl (Reinsch, *N. J. P.* 16, 135); the HCl used must not be weaker than S.G. 1·1 (Bettendorff, *Z.* [2] 5, 492). According to J. M. Scherer (*Fr.* 3, 200) the delicacies of the wet tests are as follows; $AgNO_3$ detects $\frac{1}{200,000}$ part of As, $CuSO_4$ detects $\frac{1}{13,500}$ part, H_2S detects $\frac{1}{610,000}$ part, and Reinsch's test detects $\frac{1}{120,000}$ part, or after boiling for $\frac{1}{4}$ hour $\frac{1}{250,000}$ part of As. (v.) *Marsh's test.* When *hydrogen is evolved in contact* with an acidified solution of an arsenious compound, whether by the action of zinc (Marsh, *B. J.* 17, 191; 20, 190; 22, 175), magnesium (Roussin, *J.* 1866. 801), or the electric current (Bloxam, *C. J.* 13, 14), arsenic trihydride is evolved; arsenic may be separated by passing the gas through a glass tube heated at one part, or by burning the gas in a limited supply of air and presenting a cold surface of porcelain, or thick platinum (Davy, *J.* 1858. 609), on which the arsenic condenses. The deposit of arsenic is easily soluble in HNO_3, S.G. 1·2 to 1·3; the solution contains arsenious acid (which on boiling for some time is changed to arsenic acid), it gives the characteristic yellow pp. of Ag_3AsO_3 (*v. supra*); the deposit of arsenic is also easily soluble in aqueous NaClO free from Cl; if the deposit is warmed in dry H_2S yellow As_2S_3 is produced which is not changed when warmed in a current of *dry* HCl gas. Arsenious hydride passed into aqueous $AgNO_3$ precipitates Ag, but the whole of the As remains in solution along with HNO_3 formed in the reaction, and may be detected by filtering and carefully neutralising the filtrate with dilute ammonia, when yellow Ag_3AsO_3 is produced. [SbH_3 precipitates Ag from $AgNO_3$ but the whole of the Sb is at the same time thrown down; the deposit of Sb obtained by heating, or burning, SbH_3 is insoluble in NaClO solution free from Cl, and is much less soluble than As in HNO_3Aq of S.G. 1·2 to 1·3; moreover, the solution in HNO_3Aq gives no reaction with $AgNO_3Aq$ and ammonia. The reactions of the two gases towards $AgNO_3$ solution affords a means for separating them (Husson, *C. R.* 83, 199).] The electrolytic method of preparing AsH_3 has the advantages (*a*) of avoiding the use of zinc which generally contains arsenic; (*b*) of not interfering with the subsequent testing for other metals; (*c*) of allowing the separation of antimony if present—this is done by adding a little H_2S to the liquid, whereby As_2S_3 and Sb_2S_3 are formed; the former is easily, the latter not at all, decomposed by the current (Bloxam, *C. J.* 13, 14, 338). The presence of HNO_3 prevents the formation of AsH_3 (Blondlot, *J.* 1863. 681). (vi.) ***Bettendorff's test*** (*Z.* [2] 5, 492). ***Stannous chloride in fuming HCl***, **added to a solution of** As_4O_6 **or** As_2O_5 **in the same acid, precipitates metallic As mixed with a little** SnO_2. This test is said to be extremely delicate; it may be used to detect As in presence of Sb, also to remove As from HClAq (*v.* also Hager, *J.* 1870. 966). II. *Arsenic compounds.* (i.) *Neutral silver nitrate* precipitates red-brown Ag_3AsO_4 soluble in NH_4OHAq and in HNO_3Aq, but less soluble in HNO_3Aq than Ag_3AsO_3, so that if $AgNO_3$ is mixed with a solution of an arsenite and an arsenate in HNO_3Aq, and NH_4OHAq is then added drop by drop, Ag_3AsO_4 is precipitated before Ag_3AsO_3; a solution of arsenic acid in nitric acid is precipitated by $AgNO_3$ if a few drops of a concentrated solution of an alkaline acetate are added (Avery, *Am. S.* [2] 47, 25). (ii.) *Neutral copper sulphate* precipitates bluish green $CuHAsO_4$ soluble in HNO_3Aq and in NH_4OHAq. (iii.) *An alkaline solution of magnesium sulphate*, containing enough NH_4Cl to prevent precipitation of magnesia, precipitates white $Mg(NH_4)AsO_4$; delicacy 1 part of As in 56,000 (Levol, *B. J.* 28, 130) (*cf. Estimation of Arsenic*). (iv.) *Ammonium molybdate* in excess precipitates bright yellow arseno-molybdate of ammonium from warm (not cold) solutions of arsenates containing HNO_3. (v.) *Sulphuretted hydrogen* slowly reduces arsenic to arsenious acid and then (in presence of HCl) precipitates yellow As_2S_3 mixed with S. (vi) *Marsh's test.* Arsenic compounds in solution are reduced to AsH_3 by hydrogen evolved in contact with the solution; the reduction takes place under the same conditions as, but more slowly than, the reduction of arsenious compounds (*v. supra*).

Arsenic may be reduced to arsenious compounds by such deoxidising agents as sulphurous or phosphorous acid; the reverse change may be accomplished by heating with HNO_3Aq, HClAq and $KClO_3$, &c.

Detection in cases of poisoning.—Arsenious oxide or white arsenic is the usual form in which the poison is administered. Because of the insolubility of this compound, small solid particles of it may sometimes be picked out of the food or contents of the intestine; these should be tested by reduction to metallic arsenic, &c., in the dry way. The poison is, however, usually mixed with large quantities of organic matter which must be removed or destroyed, after which the arsenic may be ppd. as As_2S_3 by long-continued passage of H_2S, the pp. may then be dissolved in warm HClAq with a crystal of $KClO_3$, free chlorine removed by warming, or the pp. may be dissolved in warm H_2SO_4Aq, and Reinsch's, or better Marsh's, test used for detecting the arsenic in solution. The organic matter may be removed by diffusion (Graham); or it may be destroyed by (*a*) treatment with warm concentrated H_2SO_4Aq, (*b*) warming with HClAq and crystals of $KClO_3$ added from time to time, (*c*) warming with HClAq and a little HNO_3Aq, (*d*) passing Cl into the liquid instead of adding $KClO_3$, (*e*) heating with HNO_3Aq till the residue is semi-pasty and yellow, adding NaOHAq till the acid is neutralised, mixing with powdered Na_2CO_3 and a little $NaNO_3$, drying in a crucible and gradually heating until the mass fuses (Wöhler; *v.* also Meyer, *A.* 66, 237). All re-

agents used must be carefully freed from arsenic; a blank experiment should be conducted with the reagents alone.[1] (Buiz a. Schulz find that certain parts of the animal organism reduce As_2O_5 and also oxidise As_4O_6; they think that the poisonous effects of As_4O_6 are due to rapid deoxidation and reoxidation, *v. B.* 12, 2199; 14, 2400; 15, 1388.)

Estimation.—I. *Gravimetric methods.* (i.) As magnesium-ammonium arsenate. Solution of $MgSO_4$ is mixed with excess of NH_4OHAq and allowed to stand for 12 hours; this liquid is added to the solution containing arsenic acid to which an excess of NH_4OHAq has previously been added. After some time the pp. is collected on a weighed filter, washed with ammonia-water, and either (*a*) dried *in vacuo* over H_2SO_4, when it has the composition $Mg.NH_4.AsO_4.6H_2O$, or (*b*) dried at 100° to 110° whereby $2(Mg.NH_4.AsO_4)H_2O$ is produced, or (*c*) strongly heated over a Bunsen lamp (temperature being gradually raised) whereby $Mg_2As_2O_7$ is formed. Method *c* is recommended by Puller (*Fr.* 10, 41), who states that the best means of converting As_2S_3 into arsenic acid is treatment with red fuming HNO_3 (*v.* also Rammelsberg, *B.* 7, 544; Wood, *Am. S.* [3] 6, 368; Macivor, *C. N.* 32, 283).—(ii.) As arsenious sulphide. Arsenates are reduced to arsenites by SO_2 solution; the arsenious solution is acidified with HClAq, and As_2S_3 is ppd. by long-continued passage of H_2S; the pp. is washed with CS_2 to remove any S which it may contain, collected on a weighed filter, and dried at 100°-110° (Puller, *Fr.* 10, 41). — (iii.) As uranyl pyroarsenate. Uranic acetate in presence of ammonium salts pps. ammonium-uranyl arsenate $NH_4.UO_2.AsO_4 + Aq$, insoluble in water and acetic acid, but soluble in mineral acids. When this pp. is washed, dried, and gradually heated to bright redness, the pyroarsenate $(UO_2)_2As_2O_7$ is obtained. This method is recommended by Puller (*l.c.*); As_2S_3 may be dissolved in HClAq + $KClO_3$, and the As ppd. after adding $NH_4.C_2H_3O_2$ and $H.C_2H_3O_2$ aq.

II. *Volumetric methods.* — (i.) By iodine. Arsenious, is converted into arsenic, acid, by iodine in presence of alkali; a solution of $NaHCO_3$ saturated in the cold and used in excess is the best alkali (Waitz, *Fr.* 10, 158).—(ii.) By potassium dichromate. Arsenites are converted into arsenates by the action of $K_2Cr_2O_7Aq$ in acid solutions; the residual $K_2Cr_2O_7$ is determined by a solution of $FeSO_4$; excess of HCl should be avoided (Kessler, *Fr.* 10, 205).—(iii.) By potassium permanganate. Arsenites are oxidised to arsenates by Mn_2O_8Aq in solutions containing H_2SO_4; an excess of $K_2Mn_2O_8$ is added, and the residual Mn_2O_8 is determined by $FeSO_4$ solution (Waitz, *l.c.*).

[1] Minute attention to detailed precautions must be observed in testing for arsenic in poisoning cases. These ... will be found in the following memoirs and ...es:—Marsh, *B. J.* 17, 191; 20, 190; 22, 175; Reg... *A. Ch.* [3] 2, 159; Fresenius a. v. Babo, *A.* 49, 287; ..., *A.* 69, 364; Schneider, *P.* 85, 433; Fyfe, *P. M.* ...; Zenger, *Fr.* 1, 391; Wöhler, a. v. Siebold, *Das ...gericht. Verfahren bei einer Arsenik-Vergiftung* (1847); ..., *Ausmittelung der Gifte* [English ed. *On Poisons*]; ...gendorff, *Die gerichtlich-chemische Ermittelung der Gifte* (...88); Duflos, *Prüfung chem. Gifte* (1867); Taylor's *...lical Jurisprudence*; Taylor *On Poisons.*

References.—**Besides the papers referred to in the article, the following older memoirs on arsenic and its compounds may be consulted:—Scheele, *Opus.* 2, 28; Bergmann, *Opus.* 2, 272; Buchholz, *S.* 15, 537; Laugier, *A. Ch.* 85, 26;** Fischer, *S.* 6, 236; 12, 155; 39, 364; Thomson, *S.* 17, 422; 29, 430; Berzelius, *A. Ch.* [2] 5, 179; 11, 225; *S.* 34, 46; *P.* 7, 1, 137; Gehlen, *S.* 15, 501; Gay Lussac, *A. Ch.* [2] 3, 136; Pfaff, *S.* 45, 95; Buchner, *S.* 45, 419; Soubeiran, *P.* 19, 991; Mitscherlich, *A. Ch.* [2] 19.

Arsenic acid and Arsenates *v.* Arsenic, acids of.

Arsenic, acids of.—(In connection with these compounds *v.* arts. Acids; Acids, Basicity of; Hydroxides.) Arsenious oxide, As_4O_6, dissolves in alkalis, forming salts from which other arsenites may be obtained; no hydrate of As_4O_6 is, however, known. The heat of solution of the oxide is negative; $[As^4O^6, Aq] = -15,100$. Arsenic oxide, As_2O_5, dissolves in water with formation of the hydrate H_3AsO_4, which crystallises from concentrated solutions as $2H_3AsO_4.H_2O$; these crystals heated to 100° lose water, and arsenic acid, H_3AsO_4, remains. By the action of heat on this acid, two other acids are produced, viz. at 140°-180° *pyroarsenic acid* $H_4As_2O_7$, and at 200° *metarsenic acid* $HAsO_3$; these acids dissolve in water with reproduction of H_3AsO_4. Each arsenic acid yields a series of salts; the *arsenates* (or ortho-arsenates), divisible into three classes of the forms MH_2AsO_4, M_2HAsO_4, and M_3AsO_4; the *pyroarsenates* $M_4As_2O_7$; and the *metarsenates* $MAsO_3$. The *pyro-* and *metarsenates* have not been much investigated, they appear to exist only as solids and to yield arsenates when brought into contact with water. Thomsen's thermal examination of the behaviour of aqueous solutions of the two oxides of arsenic towards soda shows that these solutions differ much as regards reactions and hence also as regards composition. In each case the thermal behaviour of the oxide of arsenic is compared with that of the corresponding oxide of phosphorus (the formula As_2O_3 is used as being directly comparable with P_2O_3).

x	$[As^2O^3Aq, xNaOHAq]$	Diff.		$[P^2O^3Aq, xNaOHAq]$
1	7,300			14,800
		6,500	13,700	
2	13,800			28,500
		1,200	400	
3	15,000			28,900
		600		
6	15,600			—

x	$[As^2O^5Aq, xNaOHAq]$	Diff.		$[P^2O^5Aq, xNaOHAq]$
1	14,800			15,000
		12,300	12,600	
2	27,100			27,600
		6,900	8,400	
3	34,000			36,000
		1,300	1,400	
6	35,300			37,400

The mean thermal value of the reaction which occurs when one formula-weight of soda is added to an acid is 13,500; this value is reached when 2NaOHAq is added to As_2O_3Aq, but a little more heat is produced when a third formula-weight of soda is added. The values when baryta solution is used are $[As^2O^3Aq, BaOAq] = 14,000$; $[As^2O^3Aq, 2BaOAq] = 15,600$. It seems probable that the soda reacts with

water and arsenious oxide, not with arsenious acid, to produce an arsenite $NaAsO_2.HAsO_2$, analogous to potassium arsenite, and that addition of more soda changes this either into the normal, or some other, arsenite.

I. ARSENIOUS ACID and ARSENITES (Pasteur, *A.* 68, 308; Filhol, *A.* 68, 308; Kühn, *Ar. Ph.* [2] 69, 267; Streng, *A.* 129, 238; Stein, *A.* 74, 218; Reynoso, *C. R.* 31, 68; Girard, *C. R.* 34, 918; 36, 973; Bloxam, *C. J.* 15, 281). No arsenious acid has been obtained in separate form; but an aqueous solution of the oxide As_4O_6 reacts with bases to form unstable salts the compositions of which may be well represented by regarding them as derived from one or other of the three hypothetical arsenious acids, $H_3AsO_3(=As(OH)_3)$, $HAsO_2(=AsO.OH)$, $H_4As_2O_5(=As_2O(OH)_4)$. The arsenites as a class are very easily decomposed; the ammonium salt gives off ammonia at ordinary temperatures and pressures, its aqueous solution yields pure As_4O_6 on evaporation; the potassium and sodium salts are decomposed in solution by carbon dioxide with separation of As_4O_6. CaO, BaO, and SrO, dissolve when boiled with water and As_4O_6, addition of lime- baryta- or strontia-water precipitates arsenites insoluble in water, but soluble in acids and in ammonia. Solutions of arsenites of metals which form sulphides soluble in water are decomposed by H_2S with precipitation of As_2S_3; if the metal of the arsenite forms a sulphide insoluble in water then H_2S precipitates this sulphide along with As_2S_3. Many arsenites are not, however, decomposed by metals even when the oxide of the metal of the arsenite is insoluble in potash. Insoluble arsenites are obtained by adding a soluble salt of the metal to a solution of K or Na arsenite. All arsenites, with the exception of those of the alkali metals, are partially or wholly insoluble in water; when formed they usually retain some arsenious oxide, so that it is difficult, and sometimes impossible, to obtain definite compounds of fixed composition. Most arsenites are decomposed by heat with formation of an arsenate and arsenic; heated with carbon, or with carbon and borax, the whole of the arsenic is usually separated in the metallic state. Heated with ammonium chloride, most arsenites yield $AsCl_3$ and chloride of the metal of the arsenite. Solutions of the alkaline arsenites exposed to the air absorb oxygen and produce arsenates (Fresenius, *J.* 1855. 382).

Arsenites. *Ammonium arsenites* $NH_4.AsO_2$ (Pasteur, Bloxam); $(NH_4)_4As_2O_5$ (Stein). By dissolving As_4O_6 in conc. aqueous NH_3; white lustrous prisms, very soluble in water.

Barium arsenites $Ba(AsO_2)_2$; white gelatinous pp. by adding $BaCl_2Aq$ to $KAsO_2Aq$ (Filhol). $BaH_4(AsO_3)_2$; by mixing $BaCl_2Aq$ with As_4O_6Aq and NH_3Aq (Bloxam). $Ba_2As_2O_5.4H_2O$; by dissolving As_4O_6 in BaOAq (Stein).

Calcium arsenites. Solutions of the various potassium arsenites mixed with $CaCl_2Aq$ yield pps. of varying composition (Filhol, Stein). A boiling solution of As_4O_6 added to CaOAq precipitates $Ca_3(AsO_3)_2$ (Kühn). $CaCl_2Aq$ mixed with As_4O_6Aq and NH_3Aq precipitates $Ca(AsO_2)_2$ (Simon, *P.* 40, 417). As_4O_6Aq with excess of CaOAq precipitates $Ca_2As_2O_5$ (Stein).

Cobalt arsenite. $Co_3H_6(AsO_3)_4.H_2O$; rose-red pp. produced by reaction of $KAsO_2Aq$ with $CoCl_2Aq$ in presence of NH_4ClAq.

Copper arsenites. $CuSO_4Aq + KAsO_2Aq$, or ammoniacal $CuSO_4Aq + As_4O_6Aq$, yields a light green pp. (Scheele's green) of $CuHAsO_3$; soluble in NH_3Aq with formation of H_3AsO_4 and Cu_2O; soluble in KOHAq with formation of K_3AsO_4, and Cu_2O, which precipitates; when heated, $CuHAsO_3$ evolves As and H_2O, and a mixture of CuO and copper arsenide remains. By digesting $CuCO_3$ with H_2O and As_4O_6 and evaporating the solution, a yellow-green salt, probably $Cu(AsO_2)_2$, is produced.

Iron arsenites. Ferrous arsenite $Fe_2As_2O_5$ is a greenish-white pp., soluble in NH_3Aq, obtained by mixing $FeSO_4Aq$ with As_4O_6Aq and a little NH_3Aq. Various ferric arsenites appear to exist. Freshly precipitated $Fe_2(OH)_6$ digested with conc. As_4O_6Aq containing not more than $\frac{1}{12}$ as much As_4O_6 as there is $Fe_2(OH)_6$, completely converts all the As_4O_6 into an insoluble salt (Bunsen); with less $Fe_2(OH)_6$ the whole of the As_4O_6 is not removed from solution, a basic salt, $FeAsO_3.Fe_2O_3$, is produced from which water removes some As_4O_6. A basic salt (rusty-red, hard, soluble in NaOHAq), $2FeAsO_3.Fe_2O_3.7H_2O$, is produced (*a*) by adding Fe_23SO_4Aq or Fe_2Cl_6Aq to $KAsO_2Aq$, (*b*) by oxidising $FeSO_4Aq$ by *aqua regia*, neutralising by NH_3Aq, adding a saturated solution of As_4O_6 in NaOHAq, and allowing to stand for twelve hours. Another salt, $2FeAsO_3.Fe_2O_3.5H_2O$, is obtained, as an ochre-yellow pp. drying to a brown mass, on mixing As_4O_6Aq or $KAsO_2Aq$ with $Fe_2(C_2H_3O_2)_6Aq$; water withdraws part of the acid from this salt; it is decomposed by heat, losing all its arsenious acid (Simon); only a part of its acid (Bunsen; *v.* also Grimaux, *Bl.* [2] 42, 211).

Lead arsenites. $Pb(AsO_2)_2$ is a white pp. (Filhol), melting to a yellow glass (Berzelius), obtained by adding $KAsO_2Aq$ to $Pb(C_2H_3O_2)_2Aq$. Other salts are known: $Pb_2As_2O(?)$ by precipitating $Pb(C_2H_3O_2)_2Aq$ by As_4O_6Aq and NH_3Aq (Filhol, Bloxam); $Pb_3(AsO_3)_2$, by precipitating $Pb(C_2H_3O_2)_2Aq$ by (*a*) boiling As_4O_6Aq (Kühn, Bloxam), or (*b*) As_4O_6 in NaOHAq (Streng, *A.* 129, 238).

Magnesium arsenites. A solution of As_4O_6 in excess of NH_3Aq mixed with $MgSO_4Aq$ with NH_4ClAq gives a pp. which is $Mg_3(AsO_3)_2$ (Stein), $MgHAsO_3.H_2O$ (Bloxam); heated to above 250° $Mg_2As_2O_5$ remains. Other salts appear to exist; but their composition is vague and uncertain (*v.* Filhol, *l.c.*).

Manganese arsenite. $Mn_3H_6(AsO_3)_4.2H_2O$ is a light rose-red pp. obtained by adding NH_4AsO_2Aq to $MnSO_4Aq$.

Mercury arsenites. Composition undecided. $Hg2NO_3Aq$ mixed with As_4O_6Aq gives a white pp. soluble in $KAsO_2Aq$; if excess of KOH is present Hg is precipitated. An arsenite of mercury seems to be formed by mixing $HgNO_3Aq$ with $KAsO_2Aq$, or by digesting As_4O_6Aq with Hg.

Nickel arsenite. $Ni_3H_6(AsO_3)_4H_2O$ is obtained as a greenish-white pp. on adding $KAsO_2Aq$ to $NiCl_2Aq$ containing much NH_4Cl; heated in air, this salt loses H_2O, then As_4O_6, and yellow infusible $Ni_3(AsO_4)_2$ remains.

Potassium arsenites. The acid salt $KAsO_2.HAsO_2.H_2O$ is produced by adding alcohol

to a solution of much As_4O_6 in KOHAq (Pasteur, Bloxam). By digesting this salt with K_2CO_3Aq the neutral salt $KAsO_2$ is produced (Pasteur, Filhol); by treating this with KOHAq and precipitating by alcohol the salt $K_4As_2O_5$ is formed (Bloxam). Two double salts, $KAsO_2.HAsO_2.AsOI$ and $K_2H_2.3As_2O_3.2KI$ are described by Emmet (*Am. S.* [2] 18, 583), and Harms (*A.* 91, 371), obtained by adding KIAq to As_4O_6Aq, or KIAq to $KAsO_2Aq$ containing so much $HC_2H_3O_2$ that no brown colour is produced with turmeric paper.

Silver arsenites. Ag_3AsO_3, a yellow pp. obtained by adding As_4O_6Aq neutralised by NH_3Aq to $AgNO_3Aq$ (Kühn, Filhol, Bloxam); soluble in HNO_3, $H.C_2H_3O_2$, NH_3Aq, and solutions of ammonium salts, also in KOHAq; solutions are not precipitated by KClAq, but dissolve freshly prepared AgCl. Heated alone or with alkalis it is decomposed;

$$4Ag_3AsO_3 = Ag_4O + 2Ag + 2Ag_3AsO_4 + As_2O_3$$

(Wöhler, *A.* 101, 363). Other silver arsenites are described by Harms (*l.c.*).

Sodium arsenites. None obtained pure; seem to be all very soluble in water (Pasteur, Filhol, Bloxam).

Strontium arsenite. $Sr(AsO_2)_2.4H_2O$. By mixing $SrCl_2Aq$ with $KAsO_2Aq$ and allowing to deposit crystals slowly (Stein).

Tin arsenites. Scarcely known; both stannous and stannic arsenites seem to exist.

II. Arsenic acid and Arsenates.—(Setterberg, *B. J.* 26, 206; Baumann, *Ar. Ph.* 36, 36; Kodschonbey, *J. pr.* 49, 182; Field, *C. J.* 11, 6; Uelsmann, *Zeits. f. d. ges. Naturwiss.* 23, 347; Schiff, *A.* 112, 88; Maumené, *C. R.* 58, 250; Debray, *A. Ch.* [3] 61, 419, also *C. R.* 59, 40; Lechartier, *C. R.* 65, 172; Salkowski, *J. pr.* 104, 129). The conditions of formation of the three arsenic acids, H_3AsO_4, $HAsO_3$, and $H_4As_2O_7$ have been already described (p. 305). The following thermal data are given by Thomsen (*Th.* 2, 236) $[As, O^4, H^3] = 215,630$; $[As, O^4, H^3, Aq] = 215,230$; $[As^2O^5, 3H^2O] = 6,800$; $[AsO^4H^3, Aq] = -400$; $[As^2, O^7, H^4] = 360,830$; $[As^2O^5, Aq] = 6,000$; $[As^2O^3, O^2] = 64,710$; $[As^2O^3Aq, O^2] = 78,260$. The following heats of neutralisation are also given by Thomsen (*Th.* 1, 196):

n	$[NaOHAq, nH^3AsO^4Aq]$
$\frac{1}{6}$	6,233
$\frac{1}{3}$	11,972
$\frac{1}{2}$	13,790
1	14,994
2	14,724

n	$[nNaOHAq, H^3AsO^4Aq]$	Diff.
$\frac{1}{3}$	7,362	
1	14,994	
		12,586
2	27,580	
		7,336
3	35,916	
		1,484
6	37,400	

The acid H_3AsO_4 is therefore tribasic; but as the reaction of the third formula-weight of soda is accompanied by the production of not much more than half the quantity of heat which accompanies the reaction of the first or second formula-weight, it is probable that this acid belongs to the same class of tribasic acids as phosphoric acid, which class is represented by Thomsen by the typical formula $HR(OH)_2H$ (*v.* Acids, basicity of). The relative affinity of arsenic acid (*v.* Affinity) is 21 (that of $HNO_3 = 100$) which is a little less than the value for phosphoric acid.

The acid H_3AsO_4 forms translucent crystals; the acid $H_4As_2O_7$ clear lustrous crystals; and the meta-acid $HAsO_3$ a white somewhat iridescent solid; the ortho-acid dissolves in water with disappearance of heat (*v. supra*), the other acids dissolve with production of heat and formation of the ortho-acid; $[H^4As^2O^7, Aq] = 1,300$ (Thomsen, *B.* 7, 1003).

The following facts refer to the ortho-acid H_3AsO_4.

Formation.—By action of HNO_3Aq on As or As_4O_6.

Preparation.—Arsenious oxide is suspended in water and chlorine is passed in; the solution is evaporated to dryness in a platinum dish, the temperature not being allowed to rise much above 100°; the residue is dissolved in water and evaporated slowly at 100°; after a time small needle-shaped crystals of H_3AsO_4 separate out (E. Kopp, *J. pr.* 69, 270).

Properties.—Action of heat already described (*v.* p. 305). Aqueous solution tastes sour and metallic; it burns the skin. The most concentrated solution has S.G. 2·5; the following table gives some data regarding S.G. of aqueous solutions (Schiff, *A.* 113, 183).

S.G. at 15°		Pctge. of H_3AsO_4
1·7346		67·4
„ 1·3973	„	45·0
„ 1·2350	„	30·0
„ 1·1606	„	22·5
„ 1·1052	„	15·0
„ 1·0495	„	7·5

Reactions.—1. Heated with *carbon*, many *metals*, or *potassium cyanide*, it yields arsenic.—2. Heated with *conc. hydrochloric acid* $AsCl_3$ and Cl are produced; if the S.G. of the aqueous HCl used is less than 1·04 no $AsCl_3$ is produced (Fresenius and Souchay, *Fr.* 1, 448); with acid of S.G. 1·1 traces of $AsCl_3$ are formed (Mayrhofer, *A.* 158, 326).—3. *Sulphurous acid* produces arsenious oxide and sulphuric acid (Wöhler, *A.* 30, 224).—4. *Zinc* and *iron* dissolve in aqueous H_3AsO_4 with evolution of H and AsH_3 and production of gelatinous solids (? arsenates of Zn or Fe); in presence of H_2SO_4, these metals precipitate As, and evolve H and AsH_3.—5. *Sulphydric acid* (H_2S) reduces H_3AsO_4 in solution to As_2O_3, with precipitation of S, and then throws down As_2S_3; this reaction takes place slowly at 10°–15°, but more rapidly at 60°–70°. 6. *Sodium thiosulphate solution*, in presence of HCl, produces a pp. of As_2S_5 (*q. v.*).—7. *Tungstates of potassium, ammonium, and silver* when evaporated with KH_2AsO_4 solution yield complex compounds, viz., $6WO_3.As_2O_5.3K_2O.3H_2O$; $6WO_3.As_2O_5.4(NH_4)_2O.5H_2O$; and $16WO_3.As_2O_5.6Ag_2O.11H_2O$ (Gibbs, *P. Am. A.* 15, 1; 16, 109; *v.* also Debray, *C. R.* 78, 1408; and Seyberth, *B.* 7; also Sonnenschein, *J. pr.* 53, 339, 391). Derivatives of arsenic acid in which OH is replaced by Cl, or Br, or I, are not known.

Arsenates. Arsenates are isomorphous with corresponding phosphates. The arsenates of the alkali metals, and the acid arsenates of the

alkaline earth metals, are soluble in water; they lose all their arsenic as chloride by strongly heating with sal-ammoniac (Rose, *P.* 116, 453). The neutral and basic arsenates are easily soluble in mineral acids, including arsenic acid. Debray (*l.c.*) describes a series of amorphous arsenates, $MH_2AsO_4.H_2O$, obtained by precipitating alkaline arsenates by salts of the metals M; these arsenates become crystalline, according to Debray, by long-continued digestion with the liquids in which they are produced. By fusing chlorides and fluorides with arsenates, Lechartier (*l.c.*) obtained a series of crystalline salts analogous in composition to *Wagnerite* and *Apatite*; thus:

Corresponding to *Wagnerite* [$(PO_4.F.Mg_2)$].

$AsO_4.Cl.Ca_2$
$AsO_4.Cl(F).Mg_2$
$AsO_4.Cl.Mg_2$
$AsO_4.Cl.Mn_2$

Corresponding to *Apatite* [$(PO_4)_3.Cl(F).Ca_5$].

$(AsO_4)_3.Cl.Ca_5$ $(AsO_4)_3.Cl.Sr_5$
$(AsO_4)_3.Cl(F).Ca_5$ $(AsO_4)_3.Cl.Ba_5$.
$(AsO_4)_3.Cl.Pb_5$

Debray also obtained the following crystallised insoluble arsenates by digesting arsenic acid solution with carbonates of the various metals: $2AsO_4CaH.H_2O$; AsO_4CuH; $2AsO_4CuH.3H_2O$; $(AsO_4)_2Cu_3.4H_2O$; and $AsO_4Cu.(CuOH)$. Arsenates are usually prepared by adding Na_2HAsO_4Aq to solutions of salts of the various metals, using the calculated masses of the reacting bodies.

Aluminium arsenate. White pp. by adding a soluble arsenate to a solution of an Al salt.

Ammonium arsenates. $(NH_4)_2.H_2AsO_4$; by adding NH_3Aq to conc. H_3AsO_4 until the pp. which forms is dissolved (Salkowski). $(NH_4)_3AsO_4.3H_2O$; by adding considerable excess of NH_3Aq to H_3AsO_4Aq. $NH_4H_2AsO_4$; by adding one formula-weight H_3AsO_4 to one formula-weight $(NH_4)_2HAsO_4$.

Barium arsenates. $BaHAsO_4$; crystalline, obtained by adding Na_2HAsO_4Aq to $BaCl_2Aq$. Ba_32AsO_4; crystalline, obtained by adding Na_3AsO_4Aq to $BaCl_2Aq$; acted on by water it forms the salt $BaHAsO_4$ (Field). The salt $BaH_4(AsO_4)_2$ is obtained by dissolving $BaHAsO_4$ in warm H_3AsO_4Aq and allowing to crystallise (Setterberg). Two barium-ammonium arsenates $2Ba.NH_4.AsO_4.H_2O$, and $BaH_2(NH_4)_2(AsO_4)_2$ are described (Baumann, Mitscherlich).

Bismuth arsenate. $2BiAsO_4.H_2O$; yellowish white pp. insoluble in water and HNO_3Aq, soluble in HClAq; insoluble in a conc. solution of $Bi3NO_3$ containing a little free acid (Schneider, *J. pr.* [2] 20, 418).

Cadmium arsenates. White crystalline pps. obtained by precipitating solution of Cd salts by Na_2HAsO_4Aq; two are known, $Cd_3(AsO_4)_2.3H_2O$ and $Cd_5H_2(AsO_4)_4.4H_2O$ (Salkowski).

Calcium arsenates. $Ca.H.AsO_4$; prepared like $BaHAsO_4$; occurs native as *Pharmacolite.* By treatment with NH_3Aq this salt yields $Ca_3(AsO)_4$ (Kotschonbey). Two calcium-ammonium arsenates are described, $CaH_2(NH_4)_2(AsO_4)_2$ and $CaNH_4.AsO_4.6$ or $7H_2O$ (Baumann, Kotschonbey; also Bloxam, *C. N.* 54, 163). The salt $Ca_2As_2O_7$ is obtained by strongly heating $Ca.NH_4.AsO_4.7H_2O$ (Bloxam).

Cerium arsenate. $Ce.H.AsO_4$; insoluble in water, soluble in excess of H_3AsO_4Aq.

Cobalt arsenates. $CoHAsO_4$ is unknown; $CoH_4(AsO_4)_2$ obtained by evaporating *in vacuo* solution of $CoO.H_2O$ in excess of H_3AsO_4Aq. Cobaltic arsenate, $Co_32AsO_4.8H_2O$ (Karsten, *P.* 60, 266) is a reddish powder obtained by precipitating the solution of a Co salt by Na_3AsO_4Aq; occurs native as *Cobalt-bloom.* An impure basic arsenate of cobalt is known in commerce as *Chaux métallique.*

Copper arsenates. $Cu_5H_2(AsO_4)_4.2H_2O$; obtained as a blue pp. by adding $(NH_4)_2HAsO_4Aq$ to $CuSO_4Aq$ and drying at 130° (Salkowski). $Cu_3(AsO_4)_2$ is a green powder obtained by precipitating $CuSO_4Aq$ with Na_2HAsO_4Aq; this salt dissolves in NH_3Aq, and on long standing, clear blue crystals having the composition $[(NH_3)_2Cu]_3(AsO_4)_2$ separate out (Damour, *B. J.* 26, 247; and 27, 181). Various basic arsenates of copper occur native as minerals (*v.* Coloriano, *Bl.* [2] 45, 707).

Chromium arsenates. Chromic arsenate is a green pp. obtained by mixing solutions of a chromic salt and K_3AsO_4; composition uncertain. By mixing solutions of K_2CrO_4 and H_3AsO_4 Schweizer (*J. pr.* 39, 267) obtained a gelatinous pp. having the composition (dried at 100°) $(CrO)_3AsO_4.K_2H(AsO_4)_2.4H_2O$.

Didymium arsenate.
$Di_3(AsO_4)_2.DiH(AsO_4)_2.H_2O$; by boiling H_3AsO_4Aq with Di_2O_3 (Marignac, *A. Ch.* 88, 185).

Iridium arsenate is a brown pp.

Iron arsenates. The ferrous salt is obtained by double decomposition; it oxidises easily; after drying, its composition is $Fe_2OAsO_4.5\frac{1}{3}H_2O$ (Wittstein, *Viertel-jahrsschr. pr. Pharm.* 15, 185). The ferric salt (?$FeH_3(AsO_4)_2$) is obtained by mixing Fe_2Cl_6Aq with Na_2HAsO_4Aq; it is a white powder which loses water on heating and becomes reddish, soluble in H_3AsO_4Aq, but this solution soon decomposes, unless very concentrated, depositing $Fe_2(OH)_6$ (Lunge, *Fr.* 6, 185). Various other ferric arsenates of uncertain composition have been described by Berzelius (*v.* also Grimaux, *Bl.* [2] 42, 211).

Lead arsenates. The salt $PbHAsO_4$ is obtained by double decomposition (Salkowski); when treated with NH_3Aq it yields $Pb_3(AsO_4)_2$.

Lithium arsenates. $2Li_3AsO_4.H_2O$ is a white powdery pp. obtained by dissolving Li_2CO_3 in H_3AsO_4Aq and adding NH_3Aq; when this salt is dissolved in H_3AsO_4Aq, trimetric prisms of $2LiH_2AsO_4.3H_2O$ crystallise out (Rammelsberg, *P.* 128, 311).

Magnesium arsenates. $2MgHAsO_4.13H_2O$; white pp. by mixing 5 parts Na_2HAsO_4 in solution with a dilute solution of 3 parts $MgSO_4$ (Graham, *A.* 29, 24). $Mg_3(AsO_4)_2$ is obtained by boiling the preceding salt for some time with conc. Na_2HAsO_4Aq. A magnesium-ammonium arsenate $MgNH_4AsO_4.6H_2O$ is obtained by adding H_3AsO_4Aq with excess of NH_3Aq to $MgSO_4Aq$ containing NH_4Cl; it is slightly soluble in NH_4ClAq, strongly heated it loses NH_3 and $Mg_2As_2O_7$ remains [H. Rose; Field; Wittstein; Puller; Fresenius (*Fr.* 3, 206); Levol (*A. Ch.* [3] 17, 50)]. A magnesium-potassium arsenate $MgKAsO_4$, and a corresponding sodium salt, are obtained by fusing $MgHAsO_4$ with K_2CO_3 and KOH (or Na_2CO_3 and NaOH).

Manganese arsenates. $MnHAsO_4$ is produced by saturating H_3AsO_4Aq with $MnCO_3$; using excess of H_3AsO_4Aq the salt $MnH_4(AsO_4)_2$ is formed (Schiefer). The manganese-ammonium salt $MnNH_4AsO_4.6H_2O$ is obtained like the corresponding Mg salt as a gummy pp. which becomes crystalline. Some basic Mn arsenates are described by Coloriano (*Bl.* [2] 45, 709).

Mercury arsenates. The mercurous salt Hg_2HAsO_4 is a yellowish white pp., which becomes orange red, produced by adding H_3AsO_4Aq to $HgNO_3Aq$; it is insoluble in water and $H.C_2H_3O_2Aq$, soluble in HNO_3Aq. When heated, this salt loses H_2O and Hg, and a mercuric salt (probably $Hg_2As_2O_7$) remains. By adding an excess of H_3AsO_4Aq to the mercurous salt, and evaporating, the meta-salt $Hg_2(AsO_3)_2$ is obtained as a white powder, somewhat soluble in HNO_3Aq, decomposed by HClAq with formation of HgCl, decomposed by KOHAq with withdrawal of half its arsenic as H_3AsO_4 (Simon, *P.* 41, 424).

Molybdenum arsenate is a grey pp. (for combinations of As_2O_5 with MoO_3 and K_2O *v.* ARSENIC ACID, *Reactions*, No. 7).

Nickel arsenates. Analogous to cobalt arsenates (*q. v.*). The salt $Ni_3(AsO_4)_2.8H_2O$ occurs native as *Nickel-bloom.*

Palladium arsenate is a clear yellow pp. obtained by heating Na_2HAsO_4Aq with $Pd.2NO_3Aq$.

Platinum arsenate is a light-brown pp. obtained like the Pd salt.

Potassium arsenates. The salts K_3AsO_4 and K_2HAsO_4 are obtained by adding K_2CO_3 or KOH to H_3AsO_4Aq; the former crystallises from very conc. solutions (Graham, *P.* 32, 47). By heating together equal parts of KNO_3 and As_4O_6, dissolving in water and evaporating, or by adding KOHAq to H_3AsO_4Aq until neutral to litmus and crystallising, the salt KH_2AsO_4 is obtained. The crystals of this salt are fairly soluble in water (S. 6° = 19), insoluble in alcohol. Heated above 288° the salt melts to a glassy mass.

Silver arsenates. Ag_3AsO_4 is a dark red-brown pp. produced by mixing H_3AsO_4Aq, or solution of an alkaline arsenate, with $AgNO_3Aq$; it melts to a brownish-red glass, it is decomposed by HClAq to AgCl and H_3AsO_4Aq, it is soluble in $HC_2H_3O_2Aq$, NH_3Aq, and solutions of many NH_4 salts. By digesting this salt for some time at a gentle heat with H_3AsO_4Aq a white salt, $2AgAsO_3.As_2O_5$, is obtained.

Sodium arsenates. $Na_2HAsO_4.12H_2O$, S.G. 1·67 (Schiff), is obtained in large crystals, isomorphous with common sodium phosphate, by adding a slight excess of Na_2CO_3Aq to H_3AsO_4Aq, and evaporating at a temperature not higher than 18° (Fresenius, *J. pr.* 56, 30). The crystals which form at 20° and upwards contain $7H_2O$, S.G. 1·87 (Schiff); the crystals with $12H_2O$ effloresce quickly, those with $7H_2O$ do not. The salt melts when heated forming a clear transparent liquid. At 0° a salt crystallises with $13\frac{1}{2}H_2O$ (Setterberg). The salt $NaH_2AsO_4.H_2O$ is formed in large crystals by adding Na_2CO_3Aq to H_3AsO_4Aq until the solution is no longer ppd. by $BaCl_2Aq$; isomorphous with the corresponding phosphate; S.G. 2·535 (Schiff). A solution of S.G. about 1·7 gives crystals of $NaH_2AsO_4.2H_2O$ (Joly a. Dufet, *C. R.* 102, 1391). A conc. solution of H_3AsO_4 decomposes NaClAq and $NaNO_3$ on heating. Two double salts, viz. $NaKHAsO_4.7H_2O$ (Schiff), or $9H_2O$ (Kotschonbey), and $NaNH_4HAsO_4.4H_2O$, are described (Uelsmann). The former is obtained by neutralising NaH_2AsO_4Aq by K_2CO_3Aq, the latter by mixing solutions of Na_2HAsO_4 and $(NH_4)_2HAsO_4$. The compound $Na_3AsO_4.NaF.12H_2O$ crystallises in monometric octahedra; it resembles common alum in appearance; S.G. 2·849; S. (25°) = 10·5; S. (75°) = 50. This salt is obtained by fusing together, with special precautions, 1 part As_4O_6, 4 parts Na_2CO_3, 3 parts $NaNO_3$, and 1 part CaF_2 (Briegleb, *A.* 97, 95). Two compounds of sodium arsenates with sulphates seem to exist $Na_8As_6O_{19}.2Na_2SO_4$ (Mitscherlich), and $Na_4As_2O_7.Na_2SO_4$ (Setterberg).

Strontium arsenates. By adding Na_2HAsO_4Aq to $SrCl_2Aq$ a pp. of $SrNaAsO_4.H_2O$ is obtained; the filtrate from this when evaporated gives a white pp. of $SrHAsO_4$ (Salkowski).

Tin arsenates. $2SnHAsO_4.H_2O$; a white pp. produced by adding excess of K_2HAsO_4Aq to $SnCl_2Aq$; by the reverse process the salt $Sn(SnCl)AsO_4.H_2O$ is said to be formed (Lennsen, *A.* 114, 113).

Zinc arsenate $Zn_3(AsO_4)_2.3H_2O$ is a gelatinous substance (Köttig, *J. pr.* 48, 182 and 256); the salts $ZnHAsO_4$, $ZnH_4(AsO_4)_2$, and $Zn_3(AsO_4)_2.NH_3$, are also known (*v.* also Friedel, *Bl.* [2] 5, 433).

The compositions of the remaining arsenates, which have been very slightly investigated, are expressed by the following formulæ: – *Thallium*, $Tl.AsO_4.2H_2O$. *Thorium*, $Th.HAsO_4$. *Uranium*, $(UO)_2HAsO_4.4H_2O$; the salts $(UO)_2NaAsO_4$ and $(UO)_4Cu(AsO_4)_2.8H_2O$ are also known (Werther, *A.* 68, 312). *Vanadium*, $VH_2(AsO_4)_2$. *Yttrium*, $YHAsO_4$. Arsenates of titanium and zirconium are said to have been obtained.

Arsenic, alloys of, *v.* ARSENIC, *Combinations of*, No. 9.

Arsenic, ammonio-chloride of, *v.* ARSENIC CHLORIDE, *Combinations of*, No. 2.

Arsenic, bromide of. $AsBr_3$ (*Arsenious bromide, Tribromide of arsenic*). Mol. w. 314·25. [20°–25°]. (220°). S.G. 3·66 (Boedeker, *J.* 1860. 17). V.D. 157·5. H.F. 59,100 solid As, gaseous Br (Guntz, *C. R.* 101, 161). S.V.S. 85·8.

Preparation.—1. Powdered arsenic is shaken into a retort filled with Br vapour, and the bromide is distilled from the excess of As.—2. Powdered arsenic is added to a mixture of 1 part Br with 2 parts CS_2 until the liquid is colourless; more Br is then added, followed by more As, until the colour is no longer removed on the addition of As; the liquid is then filtered and evaporated; on standing, the bromide is deposited in crystals (Nicklès, *C. R.* 68, 837; *J. Ph.* [3] 41, 142).

Properties.—Colourless deliquescent prisms with strong arsenical odour, melting to a pale yellow liquid which fumes but slightly in the air. Volatilises unchanged and yields a crystalline sublimate.

Reactions.—1. *Water*, added in small quantity, produces AsOBr and HBr (? with a little arsenious oxide) (Serullas, *S.* 55, 345); added in large quantity, decomposes it into HBr and

As_4O_6 (Serullas, *l.c.*). An aqueous solution containing HBr deposits the oxy-salts $2AsOBr.3As_2O_3.12H_2O$ and $2AsOBr.3H_2O$ (Wallace, *P. M.* [4] 17, 261).—2. *Ammonium bromide* added to a cold concentrated aqueous solution pps. six-sided tables consisting chiefly of $AsBr_3$ (Wallace, *P. M.* [4] 17, 261). — 3. *Sodium thiosulphate* at first produces AsOBr, and then As_2S_3 (Nicklès, *J. Ph.* [3] 41, 142).— 4. *Arsenious oxide* dissolves in molten $AsBr_3$; on cooling to 150° the liquid separates into two layers, the upper of which is AsOBr, and the lower probably $3AsOBr.As_2O_3$ (Wallace, *P. M.* [4] 17, 261).

Combinations.—With the *alkaline bromides* to form rather unstable crystallisable compounds (Nicklès, *l.c.*).

Arsenic, chloride of. $AsCl_3$ (*Arsenious chloride, Trichloride of arsenic, Butter of arsenic, Caustic oil of arsenic*). Mol. w. 181·11. [below 29°]. (130°·2) (Thorpe, *C. J.* 37, 352). S.G. $\frac{0°}{4}$ 2·205 (Thorpe, *l.c.*). V.D. 90·75. Volume at $t°$ = vol. at 0°
$+ \cdot 0009913 38t + \cdot 000000849t^2 + \cdot 0000000027551t^3$ (Thorpe, *l.c.*). S.H.p. ·1122; S.H.v. ·7034; H.V. 69·74 (Regnault, *J.* 1863. 77). H.F. 71,460 [solid As and gaseous Cl] (*Th.* 2, 326). R_A 49·59 (Haagen, *P.* 131, 122). S.V. 94·37 (Thorpe, *l.c.*).

Formation.—1. By distilling As_4O_6 with conc. H_2SO_4 and NaCl (Glauber in 1648; Dumas, *P.* 9, 308).—2. By distilling As_4O_6 with conc. HCl. 3. By leading dry HCl gas over powdered As_4O_6.—4. By passing dry HCl gas over gently heated powdered As_2O_5: $As_2O_5 + 10HCl = 2AsCl_3 + 2Cl_2 + 5H_2O$ (Mayrhofer, *A.* 158, 326).— 5. By adding H_2SO_4 to a solution of As_4O_6 in conc. HCl.—6. By heating As_2S_3 with $3HgCl_2$ in a retort (Ludwig, *Ar. Ph.* 97, 23).—7. By the action of S_2Cl_2 on As (Wöhler, *A.* 73, 374).— 8. By the action of PCl_5 on As_4O_6 or on As_2O_5 ($POCl_3$, and in the case of As_2O_5 free Cl, is also formed) (Hintzig and Geuther, *A.* 111, 171).

Preparation.—Coarsely powdered arsenic is heated in a retort, *dry* chlorine is then led in, and the contents of the retort are heated; the distillate is collected in a dry receiver, and freed from excess of chlorine by redistillation from arsenic, or by shaking with mercury, pouring off from the black solid which is formed, and redistilling. Or the product may be distilled upwards for some time in a current of *dry* CO_2 (Thorpe, *l.c.*).

Properties.—A colourless, oily, fuming, very poisonous, liquid; mixes with alcohol, ether, and liquid oils; it is decomposed by water (*v. infra*). Distilled with aqueous HCl, $AsCl_3$ is partly volatilised; HCl prepared from arsenic containing H_2SO_4 always therefore contains $AsCl_3$; arsenious chloride when hot dissolves phosphorus and sulphur, but they crystallise out again on cooling.

Reactions.—1. With a little *water* the solid oxychloride $AsOCl.H_2O (= As(OH)_2Cl)$ is produced (Wallace, *P. M.* [4] 16, 358). With more water, especially if hot, $AsCl_3$ is decomposed into HCl and As_4O_6, a great portion of the latter separating in the solid form.—2. With *arsenic hydride* it reacts to form HCl and As.—3. By the action of NO_2 it is converted into As_2O_5, NOCl being simultaneously produced (Geuther, *J. pr.* [2] 8, 354).

Combinations.—1. *Arsenious oxide* dissolves in boiling $AsCl_3$, and on distillation the oxychloride AsOCl (*q. v.*) is obtained (Wallace, *P. M.* [4] 16, 358).—2. *Ammonia gas* is absorbed by $AsCl_3$ with production of a white solid, $2AsCl_3.7NH_3$ according to H. Rose (*P.* 52, 62), $2AsClNH.4NH_4Cl.NH_3$ according to Pasteur (*A. Ch.* 68, 307), Michaelis suggests the formula $2As(NH_3Cl)_3.NH_3$ (*Lehrbuch der anorg. Chem.* ii. 459, [1881]); this compound is decomposed by heat, giving off NH_3 and then a white sublimate containing NH_4Cl; it is soluble in alcohol, but is decomposed by cold water with production of heat and ammonia, from the solution six-sided plates crystallise out, having the composition $As_4Cl_2N_2H_{10}O_6$, these are decomposed by conc. ammonia with production of $(NH_4)AsO_2$ which soon decomposes (Pasteur, *l.c.*).—3. *Sulphur dichloride*, SCl_2, is said to form a compound $2AsCl_3.3SCl_2$, but according to Nilson, the product of the action is merely a mixture (*J. pr.* [2] 12, 295).—4. With *alcohol* forms easily decomposed crystals of $AsCl_3.C_2H_6O$ (De Luynes, *C. R.* 50, 831).

Arsenic, fluoride of. AsF_3 (*Arsenious fluoride*). Mol. w. 131·9. (60°·4) (Thorpe, *C. J.* 37, 352). S.G. $\frac{0°}{4}$; 2·666 (Thorpe, *l.c.*). V.D. 66·1. S.V.S. 49·5.

Formation.—By heating sodium or ammonium fluoride with arsenious bromide or chloride (Macivor, *C. N.* 30, 169).

Preparation.—Equal parts of dry powdered fluorspar and arsenious oxide are heated in a leaden vessel with 5 parts conc. H_2SO_4; the distillate is collected in a dry glass receiver.

Properties.—A transparent, very volatile, fuming, liquid; it acts slowly on glass in a closed vessel, but exposed to the air it absorbs moisture with production of As_4O_6, and HF which acts on the glass. Dropped on the skin it evaporates at once but leaves a painful wound (Dumas, *A. Ch.* [2] 31, 434). It absorbs dry NH_3 in large quantities; miscible with alcohol and ether (Macivor, *l.c.*).

Reaction.—With *water* it forms a clear liquid (heat is produced) which soon decomposes to As_4O_6 and HF.

Arsenic, haloid compounds of. AsF_3 $AsCl_3$; $AsBr_3$; AsI_3 and AsI_2, (? AsI_5). All gasified, except the di- and pent- iodide, and molecular weights known; *v.* the arts. ARSENIC, FLUORIDE OF, CHLORIDE OF, BROMIDE OF, IODIDES OF, *v.* also art. HALOID COMPOUNDS.

Arsenic, hydrides of. (In connection with these compounds *v.* art. HYDRIDES.) Two hydrides are known; gaseous AsH_3, and solid $nAsH$.

I. ARSENIC TRIHYDRIDE. AsH_3 (*Arsenuretted hydrogen; Arsine*). Mol. w. 77·9. [−113°·5]. (−54°·8) (Olszewski, *Sitz. W.* 5, 127) (about −40°). V.D. 39·1 (Dumas, *A. Ch.* 33, 355). H.F. −361,700 (solid As) (Ogier, *A. Ch.* [5] 20, 5). Discovered by Scheele in 1775.

Formation.—1. By dissolving zinc or iron in dilute HClAq or H_2SO_4Aq containing As_4O_6 or As_2O_5.—2. By electrolysis of solution of As_4O_6Aq or As_2O_5Aq.—3. By the action of organic matter on many arsenic compounds; *e.g.* the action of paper on Scheele's green (the air of

rooms the paper on the walls of which is coloured with Scheele's green usually contains a little AsH_3).

Preparation.—1. By the action of water, or better very dilute HCl or H_2SO_4, on the solid alloy of As and Na which is obtained by heating Na in AsH_3 obtained by the action of acids on Zn containing As (Janowsky, *B.* 6, 216).—2. By the action of H_2SO_4 diluted with 3 times its weight of water on the alloy of As and Zn obtained by heating equal parts of finely granulated Zn and powdered As in a covered crucible (Soubeiran, *A. Ch.* [2] 23, 307; 43, 207). The gas is collected over boiled water.

Properties.—A colourless gas with repulsive odour; excessively poisonous (in working with this gas it is impossible to be too careful; more than one chemist has been killed by it, *e.g.* Gehlen in 1815). Easily decomposed by heat into its elements even when mixed with much hydrogen. By the action of the silent electric discharge it yields solid As hydride (Ogier, *A. Ch.* [5] 20, 5). Slightly soluble in water. Dry oxygen has no action at ordinary temperatures.

Reactions.—1. Heated in *air* it burns to As_4O_6 and H_2O; in a limited supply of air, to As and H_2O.—2. Mixed with *oxygen and subjected to electric discharge*, complete decomposition to As_4O_6 and H_2O occurs explosively.—3. Concentrated *acids* decompose it into its elements; conc. H_2SO_4Aq forms also As_2S_3 (Humpert, *J. pr.* 94, 392); conc. HClAq acting for some time forms also $AsCl_3$ (Napoli, *J. pr.* 64, 93).—4. Decomposed by *chlorine*, *bromine*, or *iodine*, with production of much heat and formation of haloid compounds of As.—5. *Sulphuretted hydrogen* at about 300° forms As_2S_3 and H.—6. The *haloid acids* HCl, HBr, HI, are without action on AsH_3 at ordinary temperatures.—7. Heated with *sulphur*, As_2S_3 and H_2S are produced (Jones, *C. J.* [2] 14, 618).—8. Reacts with PCl_3 to produce AsP and HCl (*v.* Arsenic, *Combinations of*, No. 8).—9. Many *metals*, *e.g.* K, Na, Sn, heated in AsH_3 form alloys with As and set free H.—10. Many *metallic oxides*, *e.g.* CuO, decompose AsH_3 when heated with it, forming arsenides and water (the quantity of AsH_3 in a gaseous mixture may be thus determined).—11. Absorbed and slowly decomposed by *alkalis*, and by *water containing oxygen or air*.—12. Many *metallic salts* in aqueous solutions absorb and decompose AsH_3; salts of metals whose oxides are easily deoxidised produce water and arsenious oxide; salts of metals whose oxides are not so easily deoxidised produce water and arsenic which is precipitated with the metal. Thus with (1) $AgNO_3$, and (2) $CuSO_4$, solution, the reactions are

(1) $24AgNO_3Aq + 4AsH_3 + 6H_2O =$
$As_4O_6Aq + 24HNO_3Aq + 24Ag$;

(2) $2AsH_3 + 3CuSO_4Aq = As_2Cu_3 + 3H_2SO_4Aq$.

Gold chloride in solution is reduced to gold, while As_4O_6 remains in solution.

References.—(Besides those in the text) Marsh, *B. J.* 17, 191; 20, 190; 22, 175; Stromeyer, *Comment. Soc. Gött.* 16, 141; Proust, *Scher. J.* 8, 285; Fischer, *P.* 9, 261; Myers, *A.* 159, 127; Parsons, *C. N.* 35, 235.

II. Solid arsenic hydride, nAsH. Mol. w. unknown. Janowsky (*B.* 6, 220) states that when potassium or sodium arsenide is decomposed by water, a solid, brown, velvet-like, compound of As and H, in the ratio As:H, separates out. When dilute acids are used in place of water, AsH_3 is evolved and As deposited. According to Ogier (*A. Ch.* [5] 20, 5), solid nAsH is produced by the action of the silent discharge on AsH_3. Older observations recorded the production of a solid compound of As and H by the action of dilute acids on arsenide of zinc (*v.* especially Wiederhold, *P.* 118, 615), but these are contradicted by Janowsky (*l.c.*). According to Blondlot (*A. Ch.* [3] 68, 186), a solid hydride of arsenic is produced (1) in a Marsh's apparatus when a little HNO_3 is present, and (2) when AsH_3 is passed into aqueous $AgNO_3$, excess of Ag is removed by adding NaCl, a drop of HNO_3Aq is added, and a piece of Zn is placed in the liquid.

Arsenic, hydroxides of. The compounds of As, O, and H, are acids; *v.* Arsenic, acids of (*v.* also arts. Acids, and Hydroxides).

Arsenic, iodides of.

I. Arsenious iodide, AsI_3 (*Triiodide of arsenic*). Mol. w. 454·59. (394° to 414°) (Carnelley a. Williams, *C. J.* 33, 283). S.G. 4·39. V.D. 227·3. S. 30·12 at 100°. H.F. solid As, gaseous I [As, I^3] = 28,800 (Guntz, *C. R.* 101, 161). S.V.S. 103·6.

Formation.—1. By subliming together 1 part As and 3 parts I in a retort arranged so that the sublimate condenses in the neck; the sublimate is treated with hot alcohol from which the AsI_3 crystallises on cooling (Bette, *A.* 33, 349).—2. By boiling 3 parts powdered As and 10 parts I with water, filtering, and evaporating (Plisson, *S.* 55, 335).—3. By acting on $AsCl_3$ with conc. HI solution [HCl is evolved] (Hautefeuille, *Bl.* [2] 7, 198).—4. By adding a concentrated solution of KI to a hot solution of As_4O_6 in HClAq (Bamberger a. Philipp, *B.* 14, 2643).

Preparation.—A saturated solution of iodine in ether is heated to boiling with excess of powdered As in a flask with an upright condenser; the liquid is filtered while hot: on cooling, well-formed crystals of AsI_3 are obtained (Wiggers, Michaelis's *Lehrbuch der anorgan. Chem.* [1881] 2, 462).

Properties and Reactions.—Lustrous, red, hexagonal, tables, $a:c = 1:2·998$ (details of cryst. form, *v.* Friedländer, *Z. K.* 3, 214). Soluble in alcohol, ether, benzene, &c.; soluble in much water; soluble without change in alcohol; decomposed by a little water with formation of $4AsOI.3As_4O_6.24H_2O$; action of boiling H_2O produces $AsOI.As_4O_6$ which deposits on cooling (Wallace, *P. M.* [4] 17, 122).

Combinations.—1. With *iodides* of the alkali metals to form very unstable compounds (Nicklès, *C. R.* 48, 237).—2. When *ammonia* is passed into a solution of AsI_3 in benzene, a bulky white pp. of $2AsI_3.9NH_3$ is produced (Bamberger a. Philipp, *B.* 14, 2643).

Reactions.—1. Heated with *oxygen*, iodine is evolved and As_4O_6 is produced.—2. Heated with *alcohol*, ethylic iodide is formed (Bamberger a. Philipp, *B.* 14, 2643).

II. Arsenic diiodide. AsI_2 (Bamberger a. Philipp, *B.* 14, 2643). Mol. w. unknown.

Preparation.—One part As is heated with 2 parts I to 230° in a sealed tube, the product is

dissolved in CS_2 in an atmosphere of CO_2, and the liquid is allowed to deposit crystals.

Properties.—Thin prisms of a dark cherry-red colour.

Reactions.—Very easily oxidised. Decomposed by water to AsI_3 and As; ($3AsI_2 = 2AsI_3 + As$).

III. Arsenic pentiodide. According to Sloan (*C. N.* 46, 194) a brown crystalline solid, containing As and I in the ratio As:5I, is obtained by heating As with a slight excess of I to 100° for some time in an atmosphere of CO_2. The body is easily decomposed to AsI_3 and I, by heat or by solution in ether or CS_2.

Arsenic, oxides of. (In connection with these compounds, *v.* art. Oxides.) Arsenic forms two well-defined oxides, arsenious oxide As_4O_6, which has been gasified; and arsenic oxide, As_2O_5, which has not been gasified: both act as anhydrides; the acid corresponding to the former is not known, but many arsenites, M_3AsO_3, have been prepared. Three arsenic acids are known corresponding in composition to the three phosphoric acids, two of these exist only as solids, they all readily lose water yielding the anhydride As_2O_5. The greyish film which forms on the surface of arsenic exposed to the air has been regarded as a suboxide, but no definite proof of the existence of an oxide with less O than As_4O_6 has been given.

I. Arsenious Oxide. As_4O_6. Mol. w. 395·36. (*Arsenic trioxide, White arsenic, Arsenious anhydride, Arsenious acid.*) Vitreous As_4O_6 melts under pressure, crystalline vaporises without melting (Wöhler, *Gm.* 4, 255). S.G. vitreous 3·698 to 3·738; cryst. 3·85 to 4·15 (*v.* Claudet, *C. J.* [2] 6, 179, and Groth, *P.* 137, 426). V.D. 198 (at white heat, V. Meyer, *B.* 12, 1117). C.E. (cubic at 40°) ·00012378 (Fizeau, *C. R.* 62, 1133). S. (13°) vitreous, 4; cryst. 1·2 to 1·3. S. (100°) 11 (Bussy, *A.* 64, 286). S. (15° standing for some days) cryst. ·28; vitreous ·92, S. (saturated at 100° and then cooled to 15°) cryst. 2·18; vitreous, 3·33 (Buchner, *J. Ph.* [3] 1, 421). S. (alcohol, 15°) cryst. ·25; vitreous, 1·06 (Girardin, *J. Ph.* [3] 46, 269). S. (ether) 0. H.F. 309,310; H.F. in aqueous solution, 294,240; $[As^4O^6,Aq] = -15,100$ (*Th.* 2, 236). S.H. cryst. ·1279. S.V.S. vitreous, 106·3, cryst. 98·9.

Occurrence.—Native, as the mineral *Arsenite* (or *Arsenolite*); whenever arsenic volatilises in contact with air, or arsenic-containing minerals are heated in air.

Preparation.—Obtained as a principal product in the roasting of arsenical pyrites, and as a secondary product in the roasting of arsenical ores of Sn, Co, Ni, or Ag. The oxide is condensed in chambers, and purified by resublimation. Extremely poisonous; doses of 0·6 gram are usually fatal (but *v.* Roscoe 'On the alleged Practice of Arsenic-eating in Styria,' *Mem. of Lit. and Phil. Soc. of Manchester*, 1860).

Properties.—Exists in three forms, *amorphous*, *regular octahedra*, and *trimetric prisms* (*a*:*b*:*c*: = ·3758:1:·35); the first passes slowly into the second form on keeping; the third is obtained under special conditions (*v. infra*). The change from amorphous to octahedral arsenious oxide is attended with production of 5,300 gram-units of heat, and that from amorphous to prismatic with 24,950 units per As_4O_6 grams (Favre; **Troost and Hautefeuille, *C. R.* 69, 48).** **Amorphous arsenious oxide** is produced by condensing the vapour on a surface slightly cooler than the temperature of volatilisation of the oxide; it is a transparent glass-like solid which gradually becomes opaque because of formation of octahedral crystals. The **octahedral** oxide is produced by cooling the vapour quickly; by crystallising either of the other forms from water; by treating the amorphous form with ammonia solution and washing with water. This form is obtained pure by fusing commercial arsenious oxide with carbonate of sodium and nitre, dissolving the arsenate of sodium so formed in water, filtering from sodium antimonate which remains, and reducing with SO_2 solution. According to H. Rose (*P.* 35, 481) a solution of 2–3 parts amorphous As_4O_6 in 12 parts boiling conc. HClAq deposits crystals of the octahedral oxide when very slowly cooled, the formation of each crystal being accompanied by a flash of light; a similar solution of the crystalline oxide does not behave in this way. The **trimetric prismatic** variety of As_4O_6 is obtained by saturating with As_4O_6, and then allowing to cool, a boiling solution of potash (Pasteur, *C. R.* 21, 474); Wöhler found this oxide in an oven in which arsenical ores had been roasted (*P.* 26, 177); Claudet found it native at San Domingos, in Portugal (*C. J.* [2] 6, 179); Kühn obtained it from a solution of Ag_3AsO_4 in HNO_3 (*J.* 1852. 378; *v.* also Uhrich, *J.* 1858. 173); Scheurer-Kestner found it in pipes leading from the pyrites burners to the chambers of a sulphuric acid works (*Bl.* [2] 10, 414). The three forms of As_4O_6 may be obtained, according to Debray (*C. R.* 58, 1209), by heating the oxide in a closed glass tube half immersed in sand, in an upright position, the lower part being at about 400°; on cooling, the lowest part of the tube contains amorphous, the middle part trimetric crystals, and the uppermost part octahedral crystals, of As_4O_6. Arsenious oxide is iso-dimorphous with antimonious oxide. The vitreous (amorphous) variety may be fused before volatilising; the crystalline sublimes without melting, even under pressure (Wöhler, *Gm.* 4, 255). The vapour is colourless and inodorous. The solubilities in water of the three forms are different (*v. supra*); long-continued contact with hot water decreases the solubility of the vitreous form inasmuch as it is thus changed to the octahedral form. Many acids dissolve As_4O_6, the vitreous more rapidly than the crystalline varieties (Bacaloglo, *J. pr.* 83, 111); from these solutions the oxide crystallises on cooling; in the case of HClAq some $AsCl_3$ remains in solution, tartaric acid is, however, said to form a salt analogous to tartar emetic. An aqueous solution of As_4O_6 slightly reddens litmus, but no acid has been obtained in definite form. The oxide must be regarded as a feebly acid-forming oxide possessing at the same time salt-forming tendencies (*v.* Arsenious acid and Arsenites; and also, *infra*, *Reactions*, especially Nos. 2, 10, and 11; and *Combinations*, No. 2).

Reactions.—Arsenious oxide acts both as a reducing and an oxidising agent; it deoxidises nitric, manganic, chromic, hypochlorous, acids, &c., with formation of arsenic acid; it oxidises carbon, sulphur, phosphorus, hydrogen, sodium,

potassium, carbon monoxide, potassium cyanide &c., when heated with these bodies. The oxide in solution is oxidised to arsenic oxide by chlorine, bromine, or iodine, in presence of alkaline bicarbonates; on this fact is based the use of As_4O_6Aq in volumetric analysis. 1. *Chlorine* passed over the dry oxide at a moderate temperature forms $AsCl_3$ (Weber, *P.* 112, 619); in solution chlorine produces arsenic acid and HClAq; *iodine* and *bromine* act similarly in presence of alkaline bicarbonates.—2. *Hydrochloric acid* forms some $AsCl_3$, but in presence of HNO_3 or $KClO_3$ only As_2O_5 is produced.—3. Free *oxygen* does not oxidise As_4O_6 at ordinary temperatures, but if a plate of Pt is partly immersed in solution of As_4O_6 in HClAq the oxygen coming off from the Pt produces As_2O_5 (Berthelot, *C. R.* 84, 1408).—4. An aqueous solution of As_4O_6 heated to 200° with *phosphorus* yields phosphide of arsenic (Oppenheim, *Bl.* [2] 1, 163).—5. *Na amalgam* appears to reduce As_4O_6Aq with production of a solution which acts as an energetic reducer (Fremy, *C. R.* 70, 61).—6. *Phosphorus trichloride* reacts at 110°-130° according to the equation $5As_4O_6Aq + 12PCl_3 = 2As_4 + 6P_2O_5Aq + 12AsCl_3Aq$ (Michaelis, *J. Z.* 6, 239).—7. *Phosphorus pentachloride* produces $AsCl_3$ and $POCl_3$ (Hurtzig a. Geuther, *A.* 111, 159).—8. When As_4O_6Aq is shaken with *ammonia solution*, an unstable compound is formed (De Luynes, *C. R.* 44, 1353).—9. *Phosphorous* and *hypophosphorous acids* precipitate arsenic and produce phosphoric acid.—10. *Sulphydric acid* (H_2S) passed into an aqueous solution of As_4O_6 forms As_2S_3 which is ppd. on addition of an acid (*v.* ARSENIOUS SULPHIDE).—11. *Ammonium hydrogen tartrate* solution is said to dissolve As_4O_6; on cooling, crystals of a double salt isomorphous with tartar emetic separate out (Marignac, *Ann. M.* [5] 15, 288). Pelouze (*A. Ch.* [3] 6, 63) describes a somewhat similar salt containing K in place of NH_4. Neither tartrate has, however, been satisfactorily examined.—12. Heated in a tube with a dry *acetate*, cacodyl oxide, $As_2(CH_3)_4O$, is produced.—13. Heated with dry *alkaline earth oxides* or with dry *carbonates of the fixed alkalis*, an arsenate of the metal is produced along with arsenic which sublimes.—14. The oxide dissolves in hot solutions of the alkalis but most of it pps. again on cooling in the air (*v.* ARSENIOUS ACID AND ARSENITES).—15. The *higher oxidised compounds of many metals* are reduced by As_4O_6; thus CuO is reduced to Cu_2O, in presence of alkali.—16. Many *metals, e.g.* zinc, reduce acid solutions of As_4O_6 with ppn. of As and formation of AsH_3.—17. As_4O_6Aq is reduced by a *Cu-Zn couple* with formation of AsH_3 (Gladstone a. Tribe, *C. J.* 33, 306).—18. *Palladium* or *platinum charged with hydrogen* separates As from As_4O_6Aq without formation of AsH_3 (Gladstone, *l.c.*).—19. Some *metallic salts which act as reducing agents* convert the oxide into arsenic; *e.g.* $SnCl_2Aq$ produces $SnCl_4$, As, and AsH_3 (Kessler, *J.* 1861, 265).—20. *Freshly ppd. ferric hydrate* reacts with As_4O_6Aq or with alkaline arsenites to form an insoluble compound, probably arsenite of iron; on this fact is based the use of ferric hydrate as an antidote in cases of arsenic poisoning (*v.* Bunsen and Berthold, *Das Eisenoxydhydrat, ein Gegengift der arsenigen Säure*, Göttingen, 1834).

Combinations.—1. Fused with *arsenic oxide* the body $As_4O_6.As_2O_5$ is probably produced (Bloxam, *C. J.* 18, 62). Other compounds of As_4O_6 and As_2O_5 are obtained by oxidising As_4O_6 by warm HNO_3Aq (*v.* Joly, *C. R.* 100, 1221).—2. Dissolves in *fuming sulphuric acid*; on evaporation yields needle-shaped crystals of $As_4O_6.4SO_3$ which are decomposed by water (Schultz-Shellac, *B.* 4, 109, gives the formula $As_2(SO_4)_3.SO_3$). A compound of As_4O_6 and SO_3 was obtained by Schafhäutl (*B. J.* 22, 113), in the fumes from copper-smelting works in Wales; and by Reich in a canal which carried off the sulphurous acid from a pyrites work near Freiberg (*J. pr.* 90, 176).—3. By cooling mixed hot aqueous solutions of KI, KBr, or KCl, and $KAsO_2$, the compounds $As_4O_6.KI$, $As_4O_6.KBr$, and $As_4O_6.KCl$, are obtained (Rüdorff, *B.* 18, 1111; *v.* also Schiff a. Sestini, *A.* 228, 72). Rüdorff (*B.* 19, 2678) also describes $NH_4I.As_4O_6$, $NH_4Br.As_4O_6$, and $2NH_4Cl.As_4O_6$. Forms a complex series of compounds with MoO_3 and WO_3 and various bases (*v.* Gibbs, *Am.* 7, 209 a. 313; *C. N.* 48, 155).

II. ARSENIC OXIDE. As_2O_5. Mol. w. unknown; not less than that represented by formula. (*Arsenic pentoxide, Arsenic anhydride.*) S.G. 3·734 (fused oxide). S.V.S. 61·6. H.F. 219,400; H.F. in aqueous solution, 225,400. $[As^2O^3Aq,O^2] = 78,350$ (*Th.* 2, 236).

Preparation.—Not produced by heating arsenic in air or oxygen. If arsenic or arsenious oxide is digested with HNO_3Aq, or with a mixture of 1 part HClAq and 12 parts HNO_3Aq in a retort, or if chlorine is led into a warm solution of As_4O_6, arsenic acid, H_3AsO_4, is produced and may be obtained as crystals by cooling a concentrated solution. When this acid is heated to low redness the anhydride As_2O_5 is produced.

Properties.—A white solid which slowly absorbs moisture from the air with formation of H_3AsO_4Aq. Slowly but completely dissolves in water forming H_3AsO_4Aq. Heated above low redness it yields As_4O_6 and O.

Reactions.—1. Heated with *charcoal, many metals*, or *potassium cyanide*, it yields As.—2. Heated with conc. *hydrochloric acid* it yields $AsCl_3$; with HCl gas even in the cold the same product is obtained (Souchay, *Fr.* 1, 189; Mayrhofer, *A.* 158, 326).—3. Reacts with *phosphorus pentachloride* thus: $As_2O_5 + 5PCl_5 = 5POCl_3 + 2Cl_2 + 2AsCl_3$ (Hurtzig a. Geuther, *A.* 3, 159).—4. According to Michaelis (*J. Z.* 6, 239), the oxide is *not acted on by $POCl_3$* even at 200°.—5. Reduced in aqueous solution by *nascent hydrogen* with formation of AsH_3; but if chlorides are present only a trace of AsH_3 is produced according to Bloxam (*C. J.* 15, 56).—6. *Stannous chloride*, in the cold, produces stannous pyroarsenate and arsenite, in warm solutions produces arsenic and AsH_3 (Schiff, *J.* 1861. 278; Kessler, *ibid.* 265).—7. With *water* it reacts to produce arsenic acid, H_3AsO_4Aq. Joly (*C. R.* 106, 1262) describes a hydrate $As_2O_5.4H_2O$. Arsenic oxide reacts as a strongly acid-forming oxide and exhibits no tendency to form corresponding salts by reactions with acids (*v. e.g.* reaction with HClAq).—8. Forms a large series of compounds with MoO_3 or WO_3 and bases (*v.* Gibbs, *Am.* 7, 209 a. 313; *C. N.* 48, 155).

Arsenic, oxybromides of. AsOBr (*Bromarsenious acid*); and ?$As_4O_5Br_2$. Mol. w. unknown, not less than represented by above formulæ.

Formation.—AsOBr is produced by the action of H_2O in limited quantity on $AsBr_3$.

Preparation.—Arsenious oxide is dissolved in molten $AsBr_3$; the dark viscid liquid which results is distilled till it becomes rather thick, and is then cooled to 150° whereat it separates into two layers, the upper of which contains the oxybromide AsOBr, and the lower probably contains the other oxybromide $A_4O_5Br_2$ (Wallace, *P. M.* [4] 17, 261).

Properties.—Brown, waxy, solid. Decomposed by heat to $AsBr_3$ and As_4O_6.

Combinations.—With *water*; a hydrate of arsenic oxybromide, $2AsOBr.3H_2O$ is obtained as thin white pearly crystals by placing a cold concentrated aqueous solution of $AsBr_3$, containing HBr, over sulphuric acid (Wallace, *l.c.*). If the solution of $AsBr_3$ in HBr is boiled, another compound, said to have the composition $4AsBr_3.11As_4O_6.24H_2O$, separates out (Wallace, *l.c.*).

Arsenic, oxychlorides of. AsOCl (*Chlorarsenious acid*); and As_3O_4Cl. Mol. ws. unknown, not less than represented by above formulæ.

Formation.—When $AsCl_3$ is mixed with less than sufficient water to completely decompose it, AsOCl is formed.

Preparation of AsOCl.—By distilling until frothing begins the liquid obtained (*a*) by dissolving As_4O_6 in boiling $AsCl_3$ in the proportion $As_4O_6:2AsCl_3$, or (*b*) by leading dry HCl gas over dry warm As_4O_6 until almost the whole of the latter has been changed to $AsCl_3$, and allowing to cool.

Properties of AsOCl.—Obtained as above, it is a hard, translucent, slightly-fuming solid which slowly absorbs oxygen from the air (Wallace, *P. M.* [4] 16, 358; Hurtzig a. Geuther, *A.* 111, 172).

Combinations.—1. A solution of $AsCl_3$ in conc. HClAq mixed with solid *ammonium chloride*, and allowed to stand, deposits crystals of $AsOCl.H_2O$, but after some days white fibrous needles are formed, which, when dried over H_2SO_4, have the composition $AsOCl.2NH_4Cl$.—2. With *water*; a hydrate of AsOCl, having the composition $AsOCl.H_2O$ ($=As(OH)_2Cl$) is obtained by adding water to $AsCl_3$ in about the proportion $8H_2O:AsCl_3$ and allowing to stand for some days. The hydrate forms small star-like crystals (Wallace, *l.c.*).

As_3O_4Cl is said to be obtained, as a hard, glass-like solid, when AsOCl is heated until As_4O_6 begins to sublime from it (about 218°) (Wallace, *l.c.*).

Arsenic, oxyiodide of. $AsOI.As_4O_6$. Mol. w. unknown. Produced in thin pearly laminæ, according to Wallace (*P. M.* [4] 17, 122) by slowly cooling a hot conc. solution of AsI_3 in H_2O, drying between filter paper, and then over H_2SO_4.

Arsenic, pentafluoride of; *double compounds containing.* No gaseous compound of arsenic of the type AsX_5, where X is a monovalent atom or atomic group, has yet been obtained. Solid compounds are, however, known, one of the constituents of which seems to be the group AsF_5. The following are described by Marignac (*A.* 145, 237):—1. *Potassic-arsenic fluoride*, $2(KF.AsF_5).H_2O$; formed in well-developed rhombic prisms by dissolving potassium arsenate in much hydrofluoric acid.—2. *Potassic-arsenic oxyfluoride*, $KF.AsOF_3.H_2O$; formed in acute rhombic plates by repeated evaporation of the solution from which compound No. 1 is obtained, or by dissolving potassium arsenate in a small quantity of HFAq.—3. *Dipotassic-arsenic fluoride.* $2KF.AsF_5.H_2O$; large, lustrous, rhombic prisms, obtained by adding KFAq to a solution in HFAq of either of the preceding salts, and evaporating.—4. *The double salt* $4KF.AsF_5.AsOF_3.3H_2O$ is said to be produced when a solution in HFAq of salt No. 3 is repeatedly evaporated.

Arsenic, phosphide of, *v.* ARSENIC, *Combinations*, No. 8.

Arsenic, selenides of, and Seleno-sulphides of, *v.* ARSENIC, *Combinations*, No. 7.

Arsenic, sulphides of. (In connection with these compounds *v.* art. SULPHIDES.) Three sulphides of arsenic are known; As_2S_2, As_2S_3, and As_2S_5. None of these has been gasified, hence the formulæ do not necessarily represent molecules of the compounds. As_2S_2 and As_2S_3 occur native as *Realgar* and *Orpiment* respectively. The two sulphides As_2S_3 and As_2S_5 are salt-forming; they dissolve in alkali sulphides with production of thio-arsenites M_3AsS_3 &c., or thio-arsenates M_3AsS_4 &c. (*v. infra*). The disulphide, As_2S_2, is not salt-forming; Berzelius's statement that it combines with various metallic sulphides has been shown to be erroneous (Nilson, *B.* 4, 989).

I. ARSENIC DISULPHIDE. As_2S_2 (*Realgar, Red orpiment, Ruby sulphur*). S.G. 3·4-3·6. H. 1·5-2. Mol. w. unknown. S.V.S. 61·1.

Occurrence.—Native, as *Realgar*, accompanying ores of silver and lead, &c.

Preparation.—1. By heating together As and S, or As_2S_3 with As, in the proper proportions.—2. By heating As_4O_6 with S, in the proportion $As_4O_6:7S$, repeatedly subliming the mass from end to end of a glass tube in a stream of CO_2 (Nilson, *J. pr.* [2] 8, 89).—3. By heating As_2S_3 with $NaHCO_3Aq$ in a closed tube to 150°; crystals are thus obtained ¼ mm. long (Sénarmont, *A. Ch.* [3] 82, 129).—4. On the large scale, impure, containing As_4O_6 (Hausmann, *A.* 74, 196), by subliming a mixture of arsenical pyrites and iron pyrites.

Properties. — Occurs native in monoclinic prisms, $a:b:c = 1·32:1:·4866$; $o = 85°16'$; orange-red, more or less translucent, resinous lustre, conchoidal fracture. Pure As_2S_2 is transparent, ruby colour, easily fusible, and crystalline after fusion; it burns in the air with a blue flame forming SO_2 and As_4O_6. It is used as a pigment, also in pyrotechny.

Reactions.—1. *Nitric acid* oxidises As_2S_2 to H_3AsO_4, H_2SO_3Aq, H_2SO_4Aq, and S.—2. Heated in a current of *chlorine*, S_2Cl_2 and $AsCl_3$ are produced (Nilson, *J. pr.* [2] 12, 295; 13, 1).—3. Heated in *hydrogen*, As and H_2S are formed (N.).—4. Solution of *potash* partially dissolves As_2S_2, with formation of As_2S_3 which then forms $KAsS_2Aq$, and production of As (N.).—5. It is slightly soluble in solutions of the *alkali-metal sulphides*.—6. It is *electrolysed* to As and S by a powerful battery (Lapschin-

Tichanowitsch, *C. C.* [2] 6, 513).—7. Heated with *iodine*, the compound $As_2S_3.AsI_3(=AsSI)$ is produced (Schneider, *J. pr.* [2] 28, 486).

II. Arsenic trisulphide. As_2S_3 (*Arsenious sulphide, Sulpharsenious anhydride, Orpiment, Yellow sulphide of arsenic*). Mol. w. unknown. S.G. 3·46–3·48. S.V.S. 70·9.

Occurrence.—Native as *Orpiment*.

Formation.—1. By heating to 70°–80° a solution of Na_2CO_3 saturated with As_2S_3 (Nilson, *J. pr.* [2] 12, 295; 13, 1).—2. Impure, commercial, by subliming together 7 parts powdered As_4O_6 with 1 part S.

Preparation.—1. By subliming together As and S in the proper proportions.—2. By saturating As_4O_6Aq with H_2S a little HClAq being added. If no mineral acid is added the As_2S_3 produced remains in solution in a colloidal form (Schneider, *J. pr.* [2] 25, 431).

Properties.—Occurs native in trimetric prisms ($a:b:c = \cdot603:1:\cdot674$) translucent, lemon- or slightly orange-yellow. Prepared in the wet way it forms a lemon-yellow powder which becomes darker when heated. Melts easily and volatilises at a higher temperature. When H_2S is passed into As_4O_6Aq, As_2S_3 is formed but remains in solution in colloidal form; a saturated solution contains 34·46 p.c. As_2S_3; it is slowly decomposed on standing, but may be boiled without precipitation of As_2S_3; bone char removes all the As_2S_3 from solution; most acids and many salts precipitate As_2S_3 (Schneider, *J. pr.* [2] 25, 431). Used as a pigment, also as a reducing agent in dyeing, also as a depilatory.

Reactions.—1. Long-continued action of *hot water* produces H_2S and As_4O_6Aq according to Field (*C. N.* 3, 114).—2. Dilute *acids* do not act on As_2S_3; conc. HClAq produces $AsCl_3$; conc. HNO_3Aq produces H_2SO_4Aq, S, and H_3AsO_4Aq. 3. Fused with *potassium-hydrogen sulphate*, SO_2 is evolved, and $KHAsO_2$ and K_2SO_4 remain. 4. *Chlorine* acts readily, a brown liquid is formed said to be a chlorosulphide of As (H. Rose); heated with chlorine, $AsCl_3$ is produced (Ludwig, *Ar. Ph.* 97, 23).—5. Passed over *hot iron, silver, &c.*, sulphide of the metal is formed, and arsenic which partially alloys with the metal.—6. Passed over *red-hot lime*, sulphide and arsenate of calcium, and arsenic are produced.—7. Heated with *sodium or potassium carbonate*, a mirror of As is obtained, along with arsenate and thio-arsenate of the alkali metal; if the *mixture is heated in hydrogen* the arsenate is reduced (Rose, *P.* 90, 565).—8. Heated with *an alkaline carbonate and charcoal or potassium cyanide*, a mirror of As is obtained; according to Fresenius (*A.* 49, 287), the whole of the As in the As_2S_3 is thus obtained; according to Rose (*Ph. C.* 1853. 594), some of the As forms thio-arsenate (KCNS being also produced) which is not reduced. No mirror of As is obtained (Rose) if As_2S_3 is mixed with excess of S and heated with KCN; the presence of an easily reduced metal is also said to prevent the formation of As, because the As alloys with the metal. If the mixture of As_2S_3 with Na_2CO_3 (or K_2CO_3) and KCN is heated in hydrogen, the whole of the arsenic is obtained as metal (comp. Rose, *P.* 90, 565, with Nilson, *A.* 49, 287).—9. As_2S_3 readily dissolves in cold *aqueous potash, soda, or ammonia*, forming an arsenite and a thio-arsenite; thus:

$$2As_2S_3 + 4KOHAq = KAsO_2Aq + 3KAsS_2Aq + 2H_2O;$$

on adding an acid to the solution the whole of the As is precipitated as As_2S_3; thus:

$$KAsO_2Aq + 3KAsS_2Aq + 4HClAq = 4KClAq + 2As_2S_3 + 2H_2O.$$

If oxide of Ag or Pb is added to a solution of As_2S_3 in NH_3Aq and the solution is boiled, the whole of the S is precipitated as Ag_2S or PbS, and Ag or Pb arsenite remains in solution. 10. When As_2S_3 is *boiled with a solution of sodium or potassium carbonate*, As_2S_3 is precipitated, CO_2 and H_2S are evolved, and the solution contains the following salts, $Na_2S.3As_2S_3$; $Na_2O.2As_2S_3O_2$; Na_3AsS_4; Na_2HAsO_4; $NaHCO_3$; (Nilson, *J. pr.* [2] 14, 1, 145).—11. As_2S_3 is easily soluble in a *hot solution of potassium-hydrogen sulphite*; thus, $2As_2S_3 + 16KHSO_3Aq = 4KAsO_2Aq + 6K_2S_2O_3Aq + 7SO_2Aq + 3S + 8H_2O$.

Combinations.—As_2S_3 acts as a salt-forming sulphide, or anhydride of a thio-acid; it combines with the sulphides of the alkali and alkaline earth metals, and with some metallic hydrosulphides, to form thio-arsenites (*q.v.* under Arsenic, thio-acids of). The following are the typical reactions:

1. $As_2S_3 + K_2SAq = 2(AsS.SKAq)$.
2. $As_2S_3 + 6NH_4HSAq = 2(As.(SNH_4)_3Aq) + 3H_2S$.
3. $As_2S_3 + 2(NH_4)_2SAq = As_2S(SNH_4)_4Aq$.

III.—Arsenic pentasulphide. As_2S_5 (*Persulphide of Arsenic*). Mol. w. unknown.

Preparation.—1. By melting As with considerable excess of S, a thin, transparent, liquid is obtained which solidifies to an elastic mass, and after some time becomes hard; if this hard solid is powdered and treated with NH_3Aq a solution of As_2S_5 is obtained from which the sulphide is thrown down on addition of HClAq (Gélis, *A. Ch.* [4] 30, 114).—2. A solution of Na_2S is digested with As_2S_3 and enough S to form As_2S_5, on evaporating and cooling large crystals of $2Na_3AsS_4.15H_2O$ are obtained (Rammelsberg, *P.* 52, 249; 90, 40); when HClAq is added to a solution of this salt, As_2S_5 is precipitated and H_2S is evolved (Fuchs, *Fr.* 1, 189; Flückiger, *Vierteljahrsschr. pr. Pharm.* 12, 330; Eckert, *ibid.* 13, 357). The product of the action of H_2S on H_3AsO_4Aq is *not* As_2S_5, as was once supposed, but is a mixture of As_2S_3 and S ($2H_3AsO_4Aq + 2H_2S = As_2O_3Aq + 5H_2O + S_2$; $As_2O_3Aq + 3H_2S = As_2S_3 + 3H_2O$) (*v.* Ludwig, *Ar. Ph.* [2] 97, 32; also H. Rose, *P.* 107, 186).

Properties.—A yellow powder, easily fusible; may be sublimed in a stream of a gas which does not act on it.

Reactions.—1. Heated in a stream of *hydrogen*, it is reduced to metallic As, and H_2S. 2. Dissolves easily in *ammonia, potash, and soda solutions*, with production of thio-arsenate, and arsenate, of the alkali metal.—3. Dissolves easily in *solutions of alkali sulphides*, forming thio-arsenates. The sulphide As_2S_5 behaves as a salt-forming compound, or as the anhydride of thio-arsenic acid; the salts which are generally formed directly from it are pyro-thio-arsenates $M_4As_2S_7$; these yield two other series of salts, viz. ortho-thio-arsenates M_3AsS_4, and *meta-thio-arsenates* $MAsS_3$ (*v.* Arsenic, thio-acids of).

Arsenic, sulpho-acids of, *v.* Arsenic thio-acids of.

Arsenic, sulpho- (or thio-) bromide of. $AsS_2Br_2 (= AsSBr.SBr_2)$. Mol. w. unknown. [−17°]. Dark red crystals deposited at −18° on addition of a small quantity of powdered As to a solution of S in Br in ratio S:Br₂; decomposed by water into As_4O_6Aq, HBrAq, and S (Hannay, *C. J.* 33, 291).

Arsenic, sulpho- (or thio-) iodide of. AsSI. Said to be formed by the mutual action of As_2S_2 and I (Schneider, *J. pr.* [2] 23, 486).

Arsenic, sulphydrates (or hydrosulphides) of. Only one compound As, S, and H is definitely known, $AsS(SH)_3$; *v. Thioarsenic acids* under Arsenic, thio-acids of (*v.* also the art. Hydrosulphides).

Arsenic, tellurides of, *v.* Arsenic, *Combinations*, No. 6.

Arsenic, thio-acids of. (In connection with these compounds *v.* the art. Hydrosulphides.) Arsenious sulphide, As_2S_3, dissolves in alkalis or alkali sulphides to form salts, and from these other salts are obtained by double decomposition. The sulphide As_2S_3 may be regarded as the anhydride of three thio-acids AsS.SH, $As(SH)_3$, and $As_2S(SH)_4$, corresponding to the three hypothetical oxy-acids (*v.* Arsenious acid); none of these acids is known, all attempts to prepare them having resulted only in the production of As_2S_3 and H_2S, but thio- or sulph- arsenites are known belonging to the three types, $MAsS_2$, M_3AsS_3, and $M_4As_2S_5$. The more important of these salts are described below. Arsenic pentasulphide, As_2S_5, dissolves in alkalis and alkali sulphides to form salts from which other salts are obtained (*v. infra*). According to Nilson (*J. pr.* [2] 14, 1, 145) the pp. obtained by adding dilute HClAq to a solution of Na_3AsS_4 (*v.* Arsenic pentasulphide, *Preparation of*) has the composition of ortho-thio-arsenic acid H_3AsS_4 [= $AsS(SH)_3$; no other thio-arsenic acid is known, but the salts may be divided into three classes, analogous to the arsenates, viz.: *pyro-thio-arsenates* $M_4As_2S_7$ (hypothetical acid = $H_4As_2S_7$), *meta-thio-arsenates* $MAsS_3$ (hypothetical acid = $HAsS_3$), and *ortho-thio-arsenates* M_3AsS_4 (acid (?) H_3AsS_4).

I. Thio-arsenites. As already stated, no thio-arsenious acid is known. The salts which have been examined belong for the most part to the type $M_4As_2S_5$; they are produced either by the direct union of As_2S_3 with metallic hydrosulphides, *e.g.* $Na_4As_2S_5$, or by ordinary double decomposition of $(NH_4)_4As_2S_5Aq$ by solutions of metallic salts, *e.g.* $Pb_2As_2S_5$. A few salts belonging to the forms $MAsS_2$ and M_3AsS_3, are also known, *e.g.* $KAsS_2$ and K_3AsS_3; they are formed by the action of alkali sulphides on As_2S_3 (comp. reactions given for Arsenic trisulphide, p. 315). The thio-arsenites of the alkali and alkaline earth metals and of magnesium are soluble in water, but the solutions are decomposed on boiling, the others are insoluble in water. Most of these salts give off all their sulphur when strongly heated out of contact with air. These salts have been chiefly investigated by Berzelius (*v. Gm.* 4, 275).

Only those salts which have been fairly satisfactorily examined are mentioned in the following brief account:—

Ammonium thio-arsenites. $(NH_4)_4As_2S_5$ is obtained by dissolving As_2S_3 in $(NH_4)_2SAq$ and adding alcohol; if NH_4HSAq is added before precipitating by alcohol the salt obtained has the composition $(NH_4)_3AsS_3$.

Barium thio-arsenites. $Ba_2As_2S_5$ is obtained as a pasty brownish-red very soluble mass by digesting As_2S_3 with BaS_2H_2Aq; from the solution alcohol throws down $Ba_3(AsS_3)_2$.

Calcium thio-arsenites. The salt $Ca_3(AsS_3)_2$ is obtained as crystals by digesting As_2S_3 with milk of lime and allowing the solution to evaporate; from the brownish mother-liquor alcohol precipitates white $Ca_3(AsS_3)_2.15H_2O$.

Lithium thio-arsenites. Closely resemble the potassium salts (*q.v.*).

Potassium thio-arsenites. The salt $KAsS_2$ may be obtained in solution by dissolving As_2S_3 in K_2SAq, but this solution decomposes on evaporation; in the solid form by heating $KAsS_2$ or by fusing As_2S_3 with K_2CO_3. By adding alcohol to a solution of As_2S_3 in K_2SAq, a white pp. of K_3AsS_3 is obtained. All these salts readily undergo change in aqueous solutions. Berzelius describes several other more or less indefinite bodies as potassium thio-arsenites.

Sodium thio-arsenites. Closely analogous to the potassium salts.

The following thio-arsenites seem also to exist; they are generally obtained from $(NH_4)_4As_2S_5Aq$ by double decomposition:— $(BiS)_4As_2S_5$; $Ce_2As_2S_5$; $Cd_2As_2S_5$; $Co_2As_2S_5$; $Cu_2As_2S_5$; $Fe_2As_2S_5$; $Au_4(As_2S_5)_3$; $Mg_2As_2S_5$; $Mn_2As_2S_5$; $Hg_2As_2S_5$; $Hg(AsS_2)_2$; $Ni_2As_2S_5$; $Sn_2As_2S_5$, $SnAs_2S_5$; $Pt_2As_2S_5$; $Ag_4As_2S_5$; $(US)_4As_2S_5$; $Zn_2As_2S_5$. Thio-arsenites of *chromium*, *molybdenum*, and *zirconium*, seem also to exist.

II. Thio-arsenates. As already stated, it is probable that ortho-thio-arsenic acid H_3AsS_4 has been prepared. The thio-arsenates may be divided into three classes, of which the three potassium salts are representatives: $K_4As_2S_7$, K_3AsS_4, and $KAsS_3$. The thio-arsenates are obtained: 1. By digesting As_2S_5 with solutions of the alkali sulphides, on cooling some As_2S_5 is precipitated.—2. By dissolving As_2S_3 in solutions of alkali-polysulphides.—3. By precipitating solutions of arsenates by H_2S, or by $(NH_4)_2SAq$; in the latter case the liquids must be boiled to remove NH_3.—4. By fusing As_2S_5 with alkali carbonates.—5. By dissolving As_2S_5 in KOHAq or NaOHaq; arsenate is formed as well as thio-arsenate. The thio-arsenates of the alkali metals are yellow or red, very soluble in water, crystallisable, fairly stable, compounds; their aqueous solutions are slowly decomposed by exposure to air. The other thio-arsenates are more easily decomposed; those of the heavy metals are insoluble in water; they are best prepared by decomposing the solution of an alkali thio-arsenate by a solution of a salt of the metal. Soluble thio-arsenates are decomposed by HClAq with precipitation of As_2S_5. The salts obtained by the methods enumerated are usually *pyro*-thio-arsenates $M_4As_2S_7$; the *meta-* and *ortho-* salts are produced from these, very frequently by the action of alcohol on their solutions; alcohol usually precipitates an *ortho-* salt and leaves a *meta-* salt in solution. The *ortho-* salts are frequently crystalline; most of the others are

amorphous. Heated in absence of air, most thio-arsenates yield thio-arsenites, and then As_2S_3 which sublimes, and a metallic sulphide which remains; some, however, are unchanged by heat alone, *e.g.* M_3AsS_4 where M = Li, K, Na. Heated in air, the thio-arsenates, as a class, give off As_2S_3 and As_4O_6, and leave a sulphate in the cases of alkaline salts, or an oxide in the cases of salts of heavy metals. The thio-arsenates have been chiefly investigated by Berzelius (*v. Gm.* 4, 275); also by Nilson (*J. pr.* [2] 12, 295; 13, 1).

The following are the thio-arsenates which have been fairly well investigated:—

Ammonium thio-arsenates. The *pyro-* salt $(NH_4)_4As_2S_7$ has not been obtained as a solid: a solution of As_2S_5 in $(NH_4)_2SAq$ probably contains this salt, it is decomposed on evaporation; alcohol precipitates the *ortho-* salt $(NH_4)_3AsS_4$ in white prismatic crystals, while the *meta-* salt NH_4AsS_3 remains in solution.

Barium thio-arsenates. A solution of $BaHAsO_4$ is decomposed by H_2S, but the pure *pyro*-thio-arsenate, $Ba_2As_2S_7$, has not been obtained; this solution is decomposed by alcohol into $Ba_3(AsS_4)_2$ which precipitates, and $Ba(AsS_3)_2$ which remains in solution.

Magnesium thio-arsenates. The *pyro-* salt $Mg_2As_2S_7$ is a yellow solid, very soluble in water; by adding $Mg(SH)_2Aq$ to this solution until H_2S ceases to come off, and evaporating *in vacuo*, crystals of $Mg_3(AsS_4)_2$ are obtained; alcohol decomposes this salt, dissolving out $Mg_2As_2S_7$.

Potassium thio-arsenates. The *pyro-* salt, $K_4As_2S_7$, is best obtained by treating K_2HAsO_4Aq with H_2S and evaporating *in vacuo*; it forms a yellow viscid mass which liquefies on exposure to the air and then crystallises in rhombic plates. By adding alcohol to a conc. solution of this salt an oily liquid is obtained which crystallises when warmed giving K_3AsS_4, and $KAsS_3$ remains in solution. A salt containing both sulphur and oxygen, $AsSO.OK.H_2O$ is described by Bouquet and Cloez (*A. Ch.* [3] 13, 44), produced by the action of H_2S on cold saturated K_2HAsO_4Aq; it may perhaps be regarded as a double compound of the hypothetical oxysulphide $As_2S_2O_3$ with K_2O, but the data are very meagre.

Sodium thio-arsenates. The *ortho-* salt $2Na_3AsS_4.15H_2O$ is obtained in large white, or yellowish, monoclinic prisms, by digesting Na_2SAq with As_2S_5, or with As_2S_3 and sufficient S to form As_2S_5, and allowing to crystallise (Fresenius, *Fr.* 1, 192). The same salt is also obtained by decomposing Na_2HAsO_4Aq by H_2S, and adding alcohol to the solution; according to the conditions under which this liquid is allowed to crystallise, crystals of varying form and somewhat varying appearance are obtained (Berzelius). The crystals are not dehydrated in dry air, but when slowly heated the salt may be obtained without water of crystallisation. It is doubtful whether the *meta-* and *pyro*-thio-arsenates have been obtained; the solution from which the *ortho-* salt is thrown down by alcohol probably contains $NaAsS_3$, and the solution before alcohol is added probably contains $Na_4As_2S_7$. The double thio-arsenate $Na_3(NH_4)_3(AsS_4)_2$ is also described by Berzelius (*l.c.*).

Besides the above salts, the following thio-arsenates seem to have been obtained in fairly definite forms: $Ca_2As_2S_7$, $Ca_3(AsS_4)_2$; $Ce_2As_2S_7$, $Ce_3(AsS_4)_2$, $Ce_4(As_2S_7)_3$; $Co_2As_2S_7$; $Au_4(As_2S_7)_3$; $Fe_4(As_2S_7)_3$, $Fe_2As_2S_7$; $Pb_2As_2S_7$, $Pb_3(AsS_4)_2$; $Mn_2As_2S_7$; $Hg_2As_2S_7$, $Hg_4As_2S_7$; $Ag_4As_2S_7$; $(US)_4As_2S_7$. Thio-arsenates of Sb, Be, Bi, Cd, Cr, Li, Ni, Pt, Sr, Y, Zn, and Zr, probably exist.

Arsenic acid and Arsenates *v.* ARSENIC, ACIDS OF.

Arsenides. Binary compounds of arsenic with more positive elements, *v.* ARSENIC, *Combinations*, No. 9.

Arsenious acids and Arsenites, *v.* ARSENIC, ACIDS OF. M. M. P. M.

ARSENIC COMPOUNDS, ORGANIC. This article is devoted to compounds in whose molecules arsenic is supposed to be directly united to carbon. They are produced by distilling alkyl iodides with an alloy of arsenic with potassium or sodium (thus MeI gives As_2Me_4, $AsMe_3$, and $AsMe_4I$—Cahours a. Riche, *C. R.* 39, 541), or by heating $AsCl_3$ with compounds of mercury with alkyls or aromatic radicles or by the action of sodium on a mixture of $AsCl_3$ and a haloid derivative. The methyl derivatives will be described first, followed by the methyl-ethyl, ethyl, phenyl, and finally by the benzyl, derivatives. The nomenclature employed is somewhat different from that used for derivatives of nitrogen. Thus the radicles AsMe, $AsMe_2$, $AsMe_3$, and $AsMe_4$ are called methyl-arsine, di-methyl-arsine, tri-methyl-arsine, and tetra-methyl arsonium respectively.

Methyl-arsine dichloride $AsMeCl_2$. (133°). At 40°-50° di-methyl arsine trichloride produces $AsMeCl_2$ thus: $AsMe_2Cl_3 = MeCl + AsMeCl_2$. Liquid which does not fume. M. sol. water but not decomposed by it. It violently attacks the mucous membrane. At −10° absorbs Cl_2 forming $AsMeCl_4$ which at 0° splits up into MeCl and $AsCl_3$ (Baeyer, *A.* 107, 257).

Methyl-arsine di-iodide $AsMeI_2$. [c. 25°]. From the oxide, AsMeO, and HI. From cacodyl and iodine (Cahours, *C. R.* 50, 1022). Yellow needles (from alcohol). Converted by H_2S into AsMeS, and by HCl into $AsMeCl_2$.

Methyl-arsine sulphide AsMeS. [110°]. From H_2S and $AsMeCl_2$. Plates (from alcohol). Insol. water. Pps. Ag, Cu, and Pb, as sulphides from their salts.

Methyl-arsine disulphide $AsMeS_2$. Formed by passing H_2S into an acidified solution of methane-arsonic acid (G. Meyer, *B.* 16, 1440).

Methyl-arsine oxide AsMeO. [95°]. Formed by action of K_2CO_3 on the chloride $AsMeCl_2$. Crystallises from CS_2 in irregular cubes, smells like Asa fœtida. M. sol. cold, v. sol. hot, water; slightly volatile in vapour of water and alcohol; v. sol. aqueous acids forming neutral solutions.

Methane arsonic acid $MeAsO(OH)_2$. From $AsMeCl_2$ and excess of moist Ag_2O. From AsMeO in aqueous solution by action of HgO. From aqueous sodium arsenite and MeI (M.). Large spear-shaped laminæ composed of small needles (from alcohol).

Salts.— BaA″, $5H_2O$: ppd. as anhydrous rhombic crystals, by adding alcohol to aqueous solution; the crystals soon change to hydrated needles. Ag_2A'': nacreous crystals which explode above 100°.—CaA″ aq.

Tetra-methyl di-arsenide As_2Me_4. *Cacodyl. Alkarsin.* Mol. w. 210. [c. −6°]. (c. 170°). V.D. 7·1 (air = 1).

Preparation.—By heating di-methyl-arsine chloride (cacodyl chloride) with zinc at 100° in bulbs filled with CO_2 (Bunsen, *P.* 40, 219; 42, 145; *A.* 37, 1; 42, 14; 46, 1).

Properties. — Stinking oil; heavier than water. Takes fire in air or in chlorine. Reduces $HgCl_2$ to mercurous chloride.

Reaction.—$As_2Me_4 + 2MeI = AsMe_4I + AsMe_2I$ (Cahours, *A.* 122, 209).

Combinations.—When gradually mixed with air, chlorine, or bromine, it forms derivatives of cacodyl, behaving like a molecule of such a metal as potassium: $(AsMe_2)_2 + Cl_2 = 2(AsMe_2)Cl$; and $(AsMe_2)_2 + O = (AsMe_2)_2O$.

Tetra-methyl-di-arsine oxide $(AsMe_2)_2O$. *Cacodyl oxide.* Mol. w. 226. [c. −25°]. (120°). S.G. $\frac{15}{}$ 1·462. V.D. 7·55 (calc. 7·83).

Formation.—Cadet's fluid (*Crell. N. Chem. Arch.* 1, 212), obtained by distilling KOAc with an equal weight of As_2O_3, is cacodyl oxide mixed with some cacodyl. HgO converts both into cacodylic acid, whence a mixture of $HgCl_2$ and fuming HCl forms cacodyl chloride. The latter is converted into cacodyl oxide by distilling with aqueous potash in a current of CO_2 (Baeyer, *A.* 107, 282): $2AsMe_2Cl + 2KHO = H_2O + 2KCl + (AsMe_2)_2O$.

Properties.—Pungent, stinking oil. Slowly oxidises in air forming cacodylic acid. Acids convert it into salts of cacodyl.

Compounds. — Forms with $HgCl_2$ a compound $(AsMe_2)_2O2HgCl_2$, crystallising in trimetric plates. S. 3·47 at 100°. Distilled with fuming HCl this forms cacodyl chloride.—$(AsMe_2)_2O2HgBr_2$.—$(AsMe_2)_2O\frac{4}{3}AgNO_3$: explodes at 100°. — $(AsMe_2)_2OPtCl_2aq$: red-brown pp. converted by KBr into $(AsMe_2)_2OPtBr_2$ aq, and by KI into $(AsMe_2)_2OPtI_2$.

Di-methyl-arsine chloride $AsMe_2Cl$. (c. 100°). V.D. 4·56 (calc. 4·85). Obtained from cacodylic acid as above; or by action of chlorine-water on cacodyl.—Heavy oil; attacks the mucous membrane; combines with Cl_2 forming $AsMe_2Cl_3$. Zn, Sn, and Fe liberate As_2Me_4.

Compounds. — $AsMe_2Cl\,CuCl$ (Bunsen).—$(AsMe_2Cl)_2PtCl_4$.

Di-methyl-arsine bromide $AsMe_2Br$: yellow oil.

Di-methyl-arsine iodide $AsMe_2I$ (160°): oil (Cahours a. Riche, *A.* 92, 364).

Di-methyl-arsine cyanide $AsMe_2Cy$. [33°]. (140°). V.D. 4·63. Prisms. Excessively poisonous.

Di-methyl-arsine sulphide $(AsMe_2)_2S$. Combines with S to form $(AsMe_2)_2S_3$ [50°].

Di-methyl-arsine fluoride $AsMe_2F$. Liquid.

Di-methyl-arsine trichloride $AsMe_2Cl_3$. Cacodyl trichloride. From PCl_5 and cacodylic acid; or from cacodyl chloride and Cl_2.

Reactions.—1. At 50° it splits up as follows: $AsMe_2Cl_3 = MeCl + AsMeCl_2$.—2. With water it forms cacodylic acid.

Di-methyl-arsinic acid $AsMe_2O(OH)$. *Cacodylic acid.* Mol. w. 138. [200°].

Formation.—From cacodyl and HgO in presence of water.

Properties.—Large prisms (from alcohol), without odour, but poisonous. V. sol. water, m. sol. alcohol, insol. ether. Not acted on by HNO_3, HCl, aqua regia, $KMnO_4$ or CrO_3.

Reactions.—1. H_3PO_2 reduces it to cacodyl oxide.—2. Aqueous H_2S forms cacodyl sulphide.—3. An alcoholic solution gives with alcoholic $HgCl_2$ a pp. of $(AsMe_2)_2O_3Hg_2Cl_2$.—4. Cacodylates are converted by dry H_2S into thio-cacodylates; *e.g.* $(AsMe_2S_2)_2Pb$.—$AsMe_2S_2Cu$.—$(AsMe_2S_2)_3Sb$.—$(AsMe_2S_2)_3Bi$.—$AsMe_2S_2Au$.

Salts.—Soluble in water, but amorphous. AgA': needles.—$AgH_2A'_3$: needles.—$AgA'AgNO_3$.

Compounds.—HCl forms a crystalline compound $(AsMe_2O_2H\,HCl)$ decomposed by water. This compound distilled in a current of HCl splits up thus: $AsMe_2O_2H\,HCl + 2HCl = AsMeCl_2 + MeCl + 2H_2O$. — HA'HF: prisms.

Tri-methyl arsine $AsMe_3$. Mol. w. 120. (c. 100°). *Formation.*—1. $2AsCl_3 + 3ZnMe_2 = 3ZnCl_2 + 2AsMe_3$ (Hofmann).—2. From $AsMe_4I$ and solid potash (Cahours, *C. R.* 49, 87).

Properties.—1. Combines directly with Cl_2, Br_2, I_2, S, and O.

Iodide $AsMe_3I_2$. Splits up on distillation into MeI and $AsMe_2I$, cacodyl iodide.—*Oxide.* $AsMe_3O$: deliquescent crystals.—*Sulphide* $AsMe_3S$: prisms (from alcohol).—*Bromide* $AsMe_3Br_2$.

Tetra-methyl-arsonium iodide $AsMe_4I$.

Formation.—1. From sodium arsenide and MeI at 180°, and treating the product $(AsMe_4IAsI_3)$ with KOH (Cahours, *C. R.* 36, 1001; *A.* 122, 192).

Properties.—Plates (from alcohol mixed with MeI).

Combinations. — $AsMe_4II_2$. — $(AsMe_4I)_2ZnI_2$.—$(AsMe_4I)_2CdI_2$.—$AsMe_4IAsI_3$.

Reactions.—1. With $ZnMe_2$ gives $AsMe_5$ (?) (Cahours).—2. KOH no action.—3. Moist Ag_2O gives $AsMe_4OH$, deliquescent alkaline crystals.—4. Ag_2SO_4 gives crystalline $(AsMe_4)_2SO_4$.—5. $AgNO_3$ forms crystalline $AsMe_4NO_3$.

Penta-methyl-arsenide $AsMe_5$. From $AsMe_4I$ and $ZnMe_2$. With iodine forms MeI and $AsMe_4I$; with HCl forms CH_4 and $AsMe_4Cl$ (Cahours).

Di-methyl-ethyl-arsine. — $AsMe_2Et$. From $AsMe_2I$ and $ZnEt_2$. Liquid (Cahours).

Methyl-di-ethyl-arsine $AsMeEt_2$. From $AsMeI_2$ and $ZnEt_2$ (Cahours).

Di-methyl-di-ethyl arsonium salts.

Iodide.—$AsMe_2Et_2I$. From cacodyl and EtI, thus: $As_2Me_4 + 2EtI = AsMe_2Et_2I + AsMe_2Cl$ (Cahours a. Riche, *C. R.* 39, 541).

Hydroxide: very deliquescent.

Chloride $AsMe_2Et_2Cl$: deliquescent needles.

Platino-chloride $(AsMe_2Et_2Cl)_2PtCl_4$.

Bromide $AsMe_2Et_2Br$: deliquescent.

Iodide $AsMe_2Et_2I$: prisms.

Periodide $AsMe_2Et_2I_3$: lustrous prisms.

Nitrate $AsMe_2Et_2NO_3$: deliquescent grains.

Sulphate $(AsMe_2Et_2)_2SO_4$: octahedra.

Ethyl-arsine iodide $AsEtI_2$. From $AsEt_2I$ and I_2 (Cahours, *C. R.* 50, 1022; *A.* 116, 367). With moist Ag_2O it forms the acid $AsEtO(OH)_2$.

Ethyl-arsine chloride $AsEtCl_2$. (156°). From $HgEt_2$ and $AsCl_3$ (La Coste, *A.* 208, 33). Liquid, m. sol. water.

Ethane arsonic acid $EtAsO(OH)_2$. From the preceding by the action of diluted HNO_3. Small crystals (from alcohol).—Ag_2A'': pearly scales.

Tetra-ethyl-di-arsenide As_2Et_4. Mol. w. 266. (185°–190°). From an alloy of arsenic and sodium on EtI (Landolt, *A.* 89, 319). Heavy stinking oil, takes fire in air. Reduces salts of silver and mercury. Unites directly with sulphur and

halogens. Alcoholic $HgCl_2$ gives a crystalline precipitate $AsEt_3Cl_22Hg_2O$(?).

Iodide $AsEt_3I$. (c. 230°). Oil.

Di-ethyl-arsinic acid $AsEt_2O(OH)$. [190°]. From $AsEt_3$ and HgO under water (Landolt, *A.* 92, 365). Large plates, soluble in water. Not attacked by HNO_3 or aqua regia.

Salts.—BaA'_2HA' 2aq. Very sol. in water, difficultly sol. in alcohol.

Tri-ethyl-arsine $AsEt_3$. Mol. w. 162. (140°–170°). S.G. $\frac{17}{}$ 1·151. V.D. 5·28 (calc. 5·62).

Formation.—1. From $AsCl_3$ and $ZnEt_2$ (Hofmann a. Cahours, *C. R.* 41, 831).—2. Together with As_2Et_4 by the action of EtI on an alloy of arsenic and sodium.—3. By distilling $AsEt_4I$ with solid potash (Landolt, *A.* 89, 322).

Properties.—Oil of disagreeable odour. Fumes strongly in air. Combines directly with non-metals. Does not reduce ammoniacal silver nitrate (difference from As_2Et_4).

Combinations.—$AsEt_3Br_2$: deliquescent.—$AsEt_3I_2$. [160°]. (190°). (Cahours a. Riche, *A.* 92, 365).—$AsEt_3S$. [c. 100°]. Prisms (from ether); pps. sulphides from solutions of metallic salts. — $(AsEt_3)_2PtCl_2$. — $(AsEt_3)_4PtCl_2$. — $(AsEt_3)_2PdCl_2$ (Cahours a. Gal, *C. R.* 71, 208).—$(AsEt_3OAsEt_3Cl_2Hg_2Cl_2$(?). — $AsEt_3AuCl$. — $AsEt_3PEt_3(C_2H_4Br)Br$.

Tri-ethyl-arsine oxide $AsEt_3O$. Formed by exposure of an ethereal solution of $AsEt_3$ to the air. An oil, insoluble in acids, except HNO_3.

Tetra-ethyl-arsonium iodide $AsEt_4I$.

Formation.—1. From $AsEt_3$ and EtI (Landolt, *A.* 89, 331).—2. Arsenic with EtI at 180° gives red needles of $AsEt_4IAsI_3$, which is then boiled with potash (Cahours a. Riche, *C. R.* 39, 546).—3. An alloy of arsenic with Zn or Cd heated with EtI gives $(AsEt_4I)_2ZnI_2$ or $(AsEt_4I)_2CdI_2$; these are boiled with potash (Cahours, *A.* 122, 200).

Properties.—Needles, v. sol. water and alcohol, insol. ether.

Reactions.—1. With moist Ag_2O, gives an alkaline hydrate.—2. Combines with I_2 forming brown needles of $AsEt_4I_3$.

Tetra-ethyl arsonium salts (Landolt, *A.* 92, 371).

Chloride $AsEt_4Cl$ 4aq: deliquescent crystals, insol. ether.—$(AsEt_4Cl)_4(BiCl_3)_2$ (Jörgensen, *J. pr.* [2] 3, 346).

Platino-chloride $(AsEt_4Cl)_2PtCl_4$: sl. sol. cold water.

Bromide $AsEt_4Br$: deliquescent mass.—$(AsEt_4Br)_3(BiCl_3)_2$.

Sulphate $AsEt_4SO_4H$: grains, v. sol. water and alcohol, sl. sol. ether.

Bromo - tetra - ethyl - arsonium bromide $(CH_2Br.CH_2)AsEt_3Br$. From ethylene bromide and $AsEt_3$ at 50° (Hofmann, *Pr.* 11, 62). Rhombic dodecahedra (from alcohol). V. sol. water, sl. sol. alcohol. Aqueous $AgNO_3$ pps. half its bromine as AgBr.

Reactions.—1. With moist Ag_2O it gives vinyl triethyl arsonium hydroxide, $C_2H_3AsEt_3(OH)$.—2. With $AsEt_3$ it gives $As_2(C_2H_4)Et_6Br_2$.—3. With *ammonia* at 100° it gives a compound $NAs(C_2H_4)Et_3H_3Br_2$. This compound and the preceding are converted by Ag_2O into oxides and thence into platinochlorides (*e.g.* $NAs(C_2H_4)Et_3H_3Cl_2PtCl_4$) and other salts.—4. $AuCl_3$ gives crystals of $AsEt_4AuCl$.—5. $PtCl_4$ gives crystals of As_2Et_6Pt (Hofmann, *A.* 103, 357).

Di-methyl-di-isoamyl-arsonium iodide $AsMe_2(C_5H_{11})_2I$. From cacodyl and iso-amyl iodide at 180°, as follows: $As_2Me_4 + 2C_5H_{11}I = AsMe_2(C_5H_{11})_2I + AsMe_2I$ (Cahours a. Riche).

Tri-propyl-arsine $AsPr_3$. At 180°, arsenic combines with PrI forming $AsPr_4IAsI_3$. Distilled with solid potash, this gives $AsPr_3$ (Cahours, *C. R.* 76, 1383). Arsenic acts similarly on isobutyl iodide at 180° (Cahours, *C. R.* 77, 1406). Calcium butyrate distilled with As_2O_3 gives a distillate resembling Cadet's liquid, probably containing the propyl homologues of cacodyl compounds (Wöhler, *A.* 68, 127). Potassium valerate distilled with As_2O_3 appears similarly to give 'butyl-cacodyl' derivatives (Gibbs, *Am. S.* [2] 15, 118).

AROMATIC DERIVATIVES.

Literature.—Michaelis, *A.* 201, 184; 207, 195; 208, 1; 233, 60; *B.* 8, 1316; 9, 1566; 10, 622; 11, 1883; 13, 2176; 14, 912; 15, 1952, 2876; 18, 42; La Coste, *A.* 184, 1; 208, 1.

Di - phenyl - di - arsenide $C_6H_5As:As.C_6H_5$. *Arseno-benzene.* [196°]. Prepared by reduction (best with phosphorous acid) of an alcoholic solution of phenyl-arsine oxide (Michaelis a. Schulte, *B.* 11, 912; 15, 1952). Yellowish needles. Sol. benzene, chloroform, and CS_2; sl. sol. alcohol, insol. water and ether. On heating it gives triphenyl-arsine and arsenic.

Reactions.—1. Heated with 1 mol. of *sulphur* phenyl-arsine sulphide is formed, with more sulphur, phenyl sulphide and As_2S_3.—2. Alcoholic NH_4HS reduces it on heating to benzene, As_2S_3, and As; HI acts in a similar manner.—3. On oxidation it gives benzene-arsonic acid.—4. Combines directly with halogens.

Di-iodide.—Ph.AsI.AsI.Ph. Yellow needles. Very unstable. Prepared by reduction of phenyl-arsine iodide (which is formed by dissolving phenyl-arsine oxide in HI).

Phenyl-arsine chloride $PhAsCl_2$ (c. 253°). Obtained in theoretical quantity by heating $AsCl_3$ (800g.) with $HgPh_2$ (70 g.). Colourless liquid with unpleasant odour; insol. water, sol. KOHAq.

Phenyl-arsine tetra-chloride $PhAsCl_4$. [45°]. Formed by passing Cl into the preceding at 0°. Yellow needles, fuming in moist air; readily decomposed into Cl_2 and $PhAsCl_2$; when heated at 150° it gives C_6H_5Cl and $AsCl_3$.

Phenyl-arsine bromide $PhAsBr_2$. (285°). S.G. $\frac{15}{}$ 2·10. Colourless liquid formed by the action of conc. HBr upon PhAsO. Gives with bromine $AsBr_3$ and PhBr.

Phenyl-arsine iodide $PhAsI_2$. Oil.

Phenyl-arsine oxide PhAsO. [120°]. Formed by treating $PhAsCl_2$ with Na_2CO_3. Crystals (from alcohol); smells like anise; insol. water; sl. sol. cold, m. sol. hot, alcohol; slightly volatile with steam. Heated with HCl it forms $PhAsCl_2$. Above its melting-point it decomposes thus:

$$3PhAsO = AsPh_3 + As_2O_3.$$

Phenyl-arsine oxy-chloride $PhAsOCl_2$. [100°]. Formed by decomposing the tetrachloride with the theoretical quantity of water; or by the union of chlorine with the oxide. Crystalline; dissolved by water, being converted into benzene arsonic acid. At 120° it splits up thus:

$$PhAsOCl_2 = PhCl + AsOCl.$$

Benzene-arsonic acid $C_6H_5AsO(OH)_2$. Formed by dissolving $PhAsCl_4$ or $PhAsOCl_2$ in water. Long columns; begins to soften at 158°, changing to an amorphous anhydride, which is re-converted by water into the acid. M. sol. cold, v. sol. hot, water.

Reactions.—1. Not affected by *reducing* or *oxidising* agents.—2. *Potash fusion* produces phenol.

Salts.—NH_4HA'': needles.—KHA'': amorphous.—$BaH_2A''_2$: needles, v. sol. water.—$CaH_2A''_2$: needles.—$CaA''2aq$.—CuA'': v. sl. sol. water.—PbA'': insol. water.

Tetra-phenyl-di-arsenide $As_2(C_6H_5)_4$. *Phenyl-cacodyl.* [135°]. Formed by reduction of tetra-phenyl-di-arsine oxide with phosphorous acid. White crystals. Sl. sol. alcohol and ether. It quickly oxidises in the air, forming di-phenyl-arsinic anhydride ($Ph_4As_2O_3$).

Di-phenyl-arsine chloride Ph_2AsCl. *Phenyl-cacodyl chloride.* (333°). S.G. $\frac{15}{}$ 1·42. Prepared by heating $HgPh_2$ with a large excess of $PhAsCl_2$ at 320°. The product is then fractionally distilled. Yellow oil, insol. water, sol. alcohol, ether, and benzene, sl. sol. aqueous alkalis. Not affected by heating with Na_2CO_3. Combines with bromine and chlorine. Conc. HNO_3 slowly converts it into di-phenyl-arsinic acid.

Di-phenyl-arsine trichloride Ph_2AsCl_3. [174°]. From the preceding and chlorine. Colourless tables (from benzene). At 200° it decomposes thus: $Ph_2AsCl_3 = PhAsCl_2 + PhCl$.

Di-phenyl-arsine chloro-bromide $Ph_2AsClBr_2$. Formed by passing dry bromine-vapour into Ph_2AsCl. Excess of Br produces di-bromo-benzene.

Tetra-phenyl-di-arsine oxide $(Ph_2As)_2O$. [92°]. Formed by heating Ph_2AsCl with alcoholic KOH.

Di-phenyl-arsine bromide Ph_2AsBr. (356°). From the oxide and HBr.

Di-phenyl-arsine oxy-chloride $(Ph_2AsCl_2)_2O$. [117°]. From the oxide and chlorine.

Di-phenyl-arsinic acid $Ph_2AsO.OH$. [174°]. S.G. 1·55. From the oxy-chloride or the tri-chloride by the action of water. White needles; sol. water and alcohol, sl. sol. benzene and ether. Not attacked by CrO_3 or boiling conc. HNO_3.

Salts.—NaA'.—NH_4A': unstable feathery crystals.—BaA'_2.—CuA'_2.—$HO.CuA'$.—AgA'.—PbA'_2.

Tri-phenyl-arsine $AsPh_3$. [59°]. (above 360°). S.G. 1·306. Prepared by heating phenyl-arsine oxide at 200°, thus: $3PhAsO = AsPh_3 + As_2O_3$. More readily by the action of sodium (50 g.) on $AsCl_3$ (54 g.) and chloro-benzene (101 g.), diluted with 4 vols. dry ether. Is also a by-product in preparing Ph_2AsCl from $PhAsCl_2$ and $HgPh_2$. Triclinic crystals isomorphous with $SbPh_3$ (Philips, *B.* 19, 1031). Insol. water and dilute acids, v. sol. hot alcohol, benzene, and ether. With $HgCl_2$ it forms leaflets of $AsPh_3HgCl_2$, whence aqueous KOH forms $AsPh_3(OH)_2$, [108°], thus: $AsPh_3HgCl_2 + 2KOH = AsPh_3(OH)_2 + 2KCl + Hg$.

Tri-phenyl-arsine chloride Ph_3AsCl_2. [171°]. From $AsPh_3$ and chlorine. Tables; decomposed at 280° into Ph_2AsCl and PhCl.

Tri-phenyl-arsine sulphide Ph_3AsS. [162°]. Prepared by digesting Ph_3As with S dissolved in CS_2; or by action of ammonium sulphide on Ph_3AsCl_2. Silky needles, insol. water and ether.

Tri-phenyl-arsine oxy-nitrate $(C_6H_5)_3As(OH)NO_3$. [84°]. Formed by adding HNO_3 to an aqueous solution of the hydroxide $(C_6H_5)_3As(OH)_2$ (Philips, *B.* 19, 1033). Long glistening needles. V. sol. alcohol, sl. sol. water.

Tri-nitro-tri-phenyl-arsine oxide $(C_6H_4.NO_2)_3AsO$. [254°]. Formed by nitration of tri-phenyl-arsine-hydrate, $(C_6H_5)_3As(OH)_2$, with HNO_3 and H_2SO_4. Nearly colourless large crystals. V. sol. acetic acid, insol. alcohol and ether.

Tri-amido-tri-phenyl-arsine $(C_6H_4.NH_2)_3As$. [c. 176°]. Formed by reduction of tri-nitro-tri-phenyl-arsine oxide $(C_6H_5.NO_2)_3AsO$ with tin and HCl in acetic acid solution (P.). Colourless crystalline solid. V. sol. alcohol and dilute acids, insol. water.

Salts.—$B'''H_3Cl_3$: crystalline solid, easily soluble in water and alcohol.—$(B'''H_3Cl_3)_2(PtCl_4)_3$: yellow pp., insol. cold water.

Tri-acetyl-derivative $(C_6H_4.NHAc)_3As$. [c. 230°]. Very sparingly soluble in alcohol, more easily in acetic acid.

Tri-*p*-ethoxy-tri-phenyl-arsine $(EtO.C_6H_4)_3As$. *Tri-phenetyl-arsine.* [89°]. Formed by the action of sodium upon a mixture of *p*-bromo-phenetol and $AsCl_3$ (Michaelis a. Weitz, *B.* 20, 52).

tri-*p*-methoxy-tri-phenyl arsine $(MeO.C_6H_4)_3As$. *Tri-anisyl-arsine.* [156°]. Obtained by the action of sodium upon a mixture of *p*-bromo-anisol and $AsCl_3$ containing some acetic ether. Transparent colourless crystals. V. sol. benzene, sl. sol. alcohol and ether. HI splits it up into di-anisyl-arsine iodide $(C_6H_4.OMe)_2AsI$ and anisol; by longer and higher heating anisol and AsI_3 are formed. By heating with an excess of $AsCl_3$ it yields anisyl-arsine chloride $C_6H_4(OMe).AsCl_2$ (Michaelis a. Weitz, *B.* 20, 48).

Di-*p*-methoxy-di-phenyl-arsine chloride $(C_6H_4.OMe)_2AsCl$ [1:4]. *Di-anisyl-arsine chloride.* [80°]. Formed by dissolving the oxide in HCl. Long thin needles. V. sol. ether, less in alcohol.

Di-methoxy-di-phenyl-arsine oxide $\{(C_6H_4.OMe)_2As\}_2O$ [1:4]. *Di-anisyl-arsine oxide. Tetra-anisyl-di-arsine oxide.* [130°]. Crystalline. Formed by the action of alkalis on the iodide which is obtained by heating tri-anisyl-arsine with HI.

***p*-Methoxy-benzene-arsine chloride** $C_6H_4(OMe).AsCl_2$ [1:4]. *p-Anisyl-arsine chloride.* (230° at 117 mm.). Colourless liquid. Formed by heating tri-anisyl-arsine $(C_6H_4.OMe)_3As$ with an excess of $AsCl_3$ at 200°. Alkalis yield the oxide $C_6H_4(OMe).AsO$, a colourless crystalline solid. It combines with Cl_2 to form $C_6H_4(OMe).AsCl_4$ which is a thick yellow liquid decomposed by water giving anisyl-arsinic acid $C_6H_4(OMe).AsO(OH)_2$.

***p*-Methoxy-benzene-arsonic acid** $(C_6H_4.OMe).AsO(OH)_2$. *Anisyl-arsinic acid.* [160°]. Formed by the action of water upon the chloride $C_6H_4(OMe).AsCl_4$. Colourless crystalline solid. Sol. hot, sl. sol. cold, water; v. sol. alcohol. On heating it gives the anhydride $C_6H_4(OMe).AsO_2$.—Ag_2A'': white pp.

Phenyl-di-methyl-arsine $PhAsMe_2$. (200°). From $ZnMe_2$ and $PhAsCl_2$. Mobile liquid, sol. alcohol and benzene, insol. water.

Phenyl-tri-methyl-arsonium iodide $PhAsMe_3I$. [244°]. From the preceding and

MeI. White needles; sol. water and alcohol, insol. ether.—$(PhAsMe_3Cl)_2PtCl_4$ [219°]; v. sol. hot water.

Di-phenyl-methyl-arsine Ph_2AsMe. (306°). From Ph_2AsCl and $ZnMe_2$ in benzene (Michaelis a. Link, *A.* 207, 199). Insol. water.

Di-phenyl-di-methyl-arsonium iodide Ph_2AsMe_2I. [190°]. From the preceding and MeI. Needles; sl. sol. cold, v. sol. hot, water. Decomposed by heat into MeI and Ph_2AsMe.—$(Ph_2AsMe_2Cl)_2PtCl_4$ [219°].

Phenyl-di-ethyl arsine $PhAsEt_2$. (240°). From $PhAsCl_2$ and $ZnEt_2$. Colourless liquid. Combines with Cl, forming $PhAsEt_2Cl_2$.

Phenyl-tri-ethyl-arsonium iodide $PhAsEt_3I$. [113°]. From the preceding and EtI at 100°. Prisms, turned yellow by sunlight; sol. water and alcohol, insol. ether. Decomposed when heated in an indifferent gas into EtI and $PhAsEt_2$. Gives with AgCl the chloride $PhAsEt_3Cl$; whence $(PhAsEt_3Cl)_2PtCl_4$. Gives with Ag_2O the hydroxide $PhAsEt_3OH$, an alkaline syrup, absorbing CO_2 from the air.

Di-phenyl-ethyl arsine Ph_2AsEt. (320°). From Ph_2AsCl and $ZnEt_2$. Colourless liquid.

Di-phenyl-ethyl-arsine chloride $Ph_2AsEtCl_2$. [137°]. From the preceding and Cl. Needles (from benzene); fumes in the air; decomposed by water.

Di-phenyl-di-ethyl-arsonium iodide Ph_2AsEt_2I. [181°]. From Ph_2AsEt and EtI. Flat white needles.

Di-phenyl-methyl-ethyl-arsonium iodide $Ph_2AsMeEtI$. [170°]. S. 1·1 at 15°; 81·4 at 100°. From Ph_2AsMe and EtI or from Ph_2AsEt and MeI. Trimetric prisms; insol. ether. Split up by heat into EtI and Ph_2AsMe.

Derivatives.—$(Ph_2AsMeEt)_2PtCl_6$. [214°].

Picrate $Ph_2AsMeEt.O.C_6H_2(NO_2)_3$. [95°]. Sl. sol. cold water.

Tolyl-arsine chloride $C_7H_7AsCl_2$.

Ortho (265°). *Para* [31°]. (267°).

From $AsCl_3$ and mercuric di-tolyl (*o-* or *p-*). Bromine converts them into di-bromo-toluenes.

Tolyl-arsine tetrachloride $C_7H_7AsCl_4$.

Tolyl-arsine oxide C_7H_7AsO.

Ortho [145°]. *Para* [156°].

From $C_7H_7AsCl_2$ and aqueous Na_2CO_3. Combine with Cl_2, forming oxy-chlorides.

Toluene arsonic acid $CH_3.C_6H_4.AsO(OH)_2$. *Ortho* [160°]. The *para* compound decomposes above 300° without previous fusion.

From the tetrachloride or the oxychloride, $C_7H_7AsOCl_2$, by treatment with water. The *ortho* acid forms a crystalline anhydride $C_7H_7AsO_2$.—Ag_2A''.—BaA''.—CaA'' (La Coste a. Michaelis, *A.* 201, 255).

Di-*p*-tolyl-arsine chloride $(C_7H_7)_2AsCl$. (c. 343°). From $C_7H_7AsCl_2$ and $Hg(C_7H_7)_2$. Liquid; not affected by aqueous Na_2CO_3. Chlorine gives $(C_7H_7)_2AsCl_3$.

Tetra-*p*-tolyl-di-arsine oxide $((C_7H_7)_2As)_2O$. [98°]. Silky needles (from ether). Obtained by boiling the preceding with alcoholic KOH.

Di-*p*-tolyl-arsinic acid $(C_7H_7)_2AsO.OH$. [167°]. Formed by boiling $(C_7H_7)_2AsCl_3$ with water. Oxidised to 'dibenzarsinic' acid.

Tri-*p*-tolyl-arsine $(C_7H_7)_3As$. [145°]. Obtained by heating C_7H_7AsO.

Tri-*p*-tolyl-arsine dichloride $(C_7H_7)_3AsCl_2$. [214°]. Not attacked by water.

***p*-Carboxy-phenyl-arsine chloride** $CO_2H.C_6H_4AsCl_2$. [158°]. From the corresponding iodide and AgCl; or from the product ($COCl.C_6H_4.AsCl_2$ (?) of the action of PCl_5 upon $CO_2H.C_6H_4.AsO(OH)_2$ by treating with water. Needles (from benzene); decomposed by water.

***p*-Carboxy-phenyl-arsine iodide** $CO_2H.C_6H_4AsI_2$. [153°]. From $CO_2H.C_6H_4.AsO(OH)_2$ by HI and P. Yellow needles (from chloroform).

***p*-Carboxy-phenyl-arsine hydroxide** $CO_2H.C_6H_4As(OH)_2$. *Benzarsenious acid.* From the preceding by heating with aqueous Na_2CO_3. Colourless needles (from water). At 145°–160° it gives off H_2O leaving the oxide $CO_2H.C_6H_4AsO$. – $Ca(C_7H_6AsO_4)_2$ Aq: plates; changing at 200° into $Ca(C_7H_4AsO_3)_2$.—$AgC_7H_4AsO_3$.

***p*-Carboxy-benzene arsonic acid** $CO_2H.C_6H_4AsO(OH)_2$. *Benzarsinic acid.* Formed by oxidising toluene arsonic acid with alkaline $KMnO_4$. Transparent interlaced needles; m. sol. water, v. sl. sol. alcohol. At 190° it becomes $CO_2H.C_6H_4AsO_2$; at 230° it gives off benzoic acid. — Ag_3A'''. — $CaHA'''$ aq. — $KH_2A'''_2$. — MeH_2A'''.

***p*-Di-carboxy-di-phenyl-arsine iodide** $(CO_2H.C_6H_4)_2AsI$. [above 280°]. From $(CO_2H.C_6H_4)_2AsO.OH$, conc. HI, and P. Converted by aqueous Na_2CO_3 into the hydroxide $(CO_2H.C_6H_4)_2AsOH$. (*Dibenzarsenious acid*).—CaA'' 2aq.

***p*-Di-carboxy-di-phenyl-arsinic acid** $(CO_2H.C_6H_4)_2AsO.OH$. *Dibenzarsinic acid.* Formed from $(C_7H_7)_2AsO.OH$ and alkaline $KMnO_4$ at 60°. Leaflets, insol. water, sl. sol. alcohol.—Me_2HA''' [above 280°].

***p*-Tri-carboxy-tri-phenyl-arsine** $(CO_2H.C_6H_4)_3As$. *Tribenzarsenious acid.* From the following acid and HI. Small colourless needles.—Na_3A''' 2aq.—Ag_3A'''.

***p*-Tri-carboxy-tri-phenyl-arsine hydroxide** $(CO_2H.C_6H_4)_3As(OH)_2$. *Tribenzarsinic acid.* From tri-tolyl-arsine and alkaline $KMnO_4$.—$(CO_2K.C_6H_4)_3AsO$.

Benzyl-arsine chloride $PhCH_2AsCl_2$. (175°) at 50mm. Formed by heating tri-benzyl-arsine with excess of $AsCl_3$. Easily oxidised by air: $PhCH_2AsCl_2 + O = PhCH_2Cl + AsOCl$.

Di-benzyl-arsinic acid $(Ph.CH_2)_2AsO.OH$ [210°].

Preparation.—Sodium [50 g.] acting upon a solution of benzyl chloride (100 g.) and $AsCl_3$ (72 g.) in dry ether (500 g.) containing acetic ether (5 g.) forms $(PhCH_2)_3As$, $(PhCH_2)_2AsCl_3$, and $(PhCH_2)_3AsCl_2$. Alcohol extracts the first, and converts the two latter into $(PhCH_2)_2AsCl(OH)_2$ and $(PhCH_2)_3AsCl(OH)$ respectively, and they are then converted by aqueous NaOH into $(PhCH_2)_2AsO.ONa$ and $(PhCH_2)_3AsO$ (Michaelis a. Paetoff, *A.* 233, 60).

Properties.—Pearly white plates (from alcohol); attacks the mucous membrane; v. sol. hot alcohol, m. sol. hot water, sl. sol. ether. When strongly heated it gives benzoic aldehyde and dibenzyl.

Salts.—BaA'_2 8aq.—CaA'_2 6aq.—AgA'.

Reactions.—1. Conc. HCl forms $AsCl_3$ toluene, and benzyl chloride.—2. Boiling dilute HNO_3 has no effect; HNO_3 of S.G. 1·3 forms a compound $(PhCH_2)_2As(OH)_2NO_3$ [129°]; conc

HNO_3 forms benzoic and arsenic acids.—3. Combines with HCl forming $(PhCH_2)_2AsCl(OH)_2$ which crystallises from aqueous HCl in needles [128°]; this is decomposed by more water, giving $(PhCH_2)_2AsO.OH$ again.—4. HBr forms $(PhCH_2)_2AsO(OH)HBr$.

Di-benzyl-thio-arsinic acid $(PhCH_2)_2AsO.SH$. [199°]. From di-benzyl-arsinic acid and H_2S in alkaline solution.

Tri-benzyl-arsine $(PhCH_2)_3As$. [104°]. The preparation is described under di-benzyl-arsinic acid (*v. sup.*). Monoclinic needles (from alcohol). Insol. water; v. sol. ether, benzene, and glacial acetic acid; sl. sol. cold alcohol. Like $AsMe_3$, but unlike $AsPh_3$, it combines with alkyl iodides. It is not affected by boiling conc. HCl. It combines with S and halogens. Boiling dilute HNO_3 forms benzoic and arsenic acids. An ethereal solution gives with an ethereal solution of $HgCl_2$ a pp. of $(PhCH_2)_3AsHgCl_2$ [159°].

Tri-benzyl-arsine oxide $(PhCH_2)_3AsO$. [220°]. From tri-benzyl-arsine chloride or oxychloride by treatment with alkalis; or together with di-benzyl-arsinic acid by the action of wet ether upon the product of the action of sodium upon benzyl chloride and $AsCl_3$. Prisms (from dilute alcohol); v. e. sol. alcohol, sl. sol. water and ether.

Tri-benzyl-arsine oxy-chloride $(PhCH_2)_3AsCl(OH)$. [163°]. Formed by union of HCl with the preceding. V. e. sol. alcohol; insol. dilute HCl.

Tri-benzyl-arsine oxy-bromide $(PhCH_2)_3AsBr(OH)$. [120°]. Tables (from alcohol).

Tri-benzyl-arsine iodide $(PhCH_2)_3AsI_2$. [c. 95°]. Formed in impure condition by action of aqueous HI on the oxide. Converted by alcohol into the oxy-iodide, $(PhCH_2)_3AsI(OH)$ aq [78°].

Tri-benzyl-arsine-oxy-nitrate $(PhCH_2)_3As(NO_3)(OH)$. [170°]. Slender needles (from alcohol).

Tri-benzyl-arsine sulphide $(PhCH_2)_3AsS$. [214°]. Prisms (from glacial HOAc). Insol. alcohol and ether.

Tri-benzyl-methyl-arsonium iodide $(PhCH_2)_3AsMeI$. [143°]. From $(PhCH_2)_3As$ and MeI at 100°. Slender needles (from water). Gives with moist Ag_2O the alkaline hydroxide, $(PhCH_2)_3AsMe(OH)$.

Tri-benzyl-methyl-arsonium chloride $(PhCH_2)_3AsMeCl$. [201°]. — *Platinochloride* $((PhCH_2)_3AsMe)_2PtCl_6$. [173°].

Tri-benzyl-ethyl-arsonium iodide $(PhCH_2)_3AsEtI$. [148°]. White plates (from water).

Tri-benzyl-propyl-arsonium iodide $(PhCH_2)_3AsPrI$. [146°]. The isomeride, $(PhCH_2)_3AsPrI$ melts at [143°].

Tri-benzyl-isoamyl-arsonium iodide $(PhCH_2)_3As(C_5H_{11})I$. [146°].

Tetra-benzyl-arsonium chloride $(PhCH_2)_4AsCl$. [160°]. From $(PhCH_2)_3As$ and $PhCH_2Cl$ at 170°. Triclinic crystals containing aq (from water); insol. dilute HCl. Converted by aqueous KBr into the bromide $(PhCH_2)_4AsBr$, [173°], and by aqueous KI into the iodide, $(PhCH_2)_4AsI$, [168°], which forms a periodide, $(PhCH_2)_4AsI_3$, [150°]. Moist Ag_2O forms an alkaline hydroxide, split up by heat thus: $(PhCH_2)_4AsOH = PhCH_3 + (PhCH_2)_3AsO$.

Platinochloride $((PhCH_2)_4As)_2PtCl_6$.

Di-naphthyl di-arsenide $C_{10}H_7As:As.C_{10}H_7$. *Arseno-naphthalene*. [221°]. Prepared by heating an alcoholic solution of naphthyl-arsine oxide with phosphorous acid (Michaelis a. Schulte, *B.* 15, 1954). Slender yellow needles; sl. sol. alcohol, benzene, CS_2 and chloroform; insol. water and ether. Converted by Cl into $C_{10}H_7AsCl_2$. With sulphur it gives $C_{10}H_7AsS$. It is oxidised by HNO_3 to naphthalene arsonic acid.

Naphthyl-arsine chloride $C_{10}H_7AsCl_2$. [63°]. From mercury di-naphthyl and $AsCl_3$. Crystalline powder; insol. water, v. sol. alcohol.

Naphthyl-arsine oxide $C_{10}H_7AsO$. [245°]. From the preceding by treatment with aqueous Na_2CO_3. Powder; sl. sol. alcohol, ether, and water. On dry distillation it gives C, As, and naphthalene.

Naphthalene arsonic acid $C_{10}H_7AsO(OH)_2$. [197°]. Needles. Formed by action of water on $C_{10}H_7AsCl_4$, which is obtained by treating $C_{10}H_7AsCl_2$ with chlorine (W. Kelbe, *B.* 11, 1503).

ASAFŒTIDA. A gum-resin obtained by drying the juice contained in the root of *Ferula asafœtida*, a Persian plant. Potash fusion gives resorcin and protocatechuic acid. Asafœtida contains ferulic acid (*q. v.*), but its odour is due to 3 p.c. of an essential oil (135°–140°) which appears to be a mixture of $C_{12}H_{22}S$ and $C_{12}H_{22}S_2$. Its alcoholic solution is ppd. by $HgCl_2$ (Pelletier, *Bull. Pharm.* 3, 556; Johnston, *P. M.* Dec. 1838; Hlasiwetz, *A.* 71, 23).

ASARITE.—Impure asarone.

ASARONE $C_{12}H_{16}O_3$. [59°]. (296°). S.G. $\frac{18}{}$ 1·165. Contained in the root of *Asarum europæum*. Needles or plates; v. sol. alcohol, ether, and glacial HOAc, sl. sol. hot water (Blanchet a. Sell, *A.* 6, 296; C. Schmidt, *A.* 53, 156; Butlerow a. Rizza, *B.* 17, 1159; *Bl.* [2] 43, 114; Pollock, *B.* 17, 1415).

ASCLEPIONE $C_{20}H_{34}O_3$. [104°]. Extracted by ether from the coagulum got by heating the milky juice of *Asclepias syriaca*. Radiating crystals; insol. water and alcohol. Not attacked by boiling KOHAq (List, *A.* 69, 125; Gram, *C. C.* 1886, 735).

ASEBOTOXIN. C. 60·5 p.c.; H. 7·4 p.c.; O. 32·1 p.c. [120°]. A glucoside extracted by water from the leaves of *Andromeda japonica*. Brittle mass. The addition of conc. HCl to its alcoholic solution gives a blue colour (Eijkman, *R.* 1, 224; *Ph.* [3] 13, 365). It is accompanied by a glucoside, asebotin $C_{24}H_{28}O_{12}$, crystallising in yellow needles [147·5°] and also by asebo-quercetin $C_{24}H_{16}O_{11}$ and asebofuscin $C_{18}H_{18}O_8$ (Eijkman, *J.* 1883, 1410; *R.* 2, 99, 200).

ASH OF ORGANIC BODIES.

The inorganic constituents contained in vegetable and animal products are usually determined by incineration of the substance, and determination of the weight and composition of the ash. The first question to be considered is—Does this ash accurately represent the inorganic constituents of the substance?

The sulphuric acid originally present is undoubtedly but imperfectly represented. The tendency to the reduction of sulphates to sulphides during ignition with carbonaceous, and especially with nitrogenous, matter, is generally overborne by the oxidation of the sulphur contained in the albuminoids. The sulphuric acid found in the ash is thus greater

than that originally present; it entirely fails, however, to represent the sulphur present in the original substance; this must be determined by a special experiment.

The carbonic acid originally present in the substance is generally quite undiscoverable by an analysis of the ash. Carbonic acid may be lost by the decomposition of calcium and magnesium carbonates during ignition; or by the decomposition of carbonates by the action of silica, or of phosphates containing less than three equivalents of base. On the other hand carbonates are produced when tribasic alkali phosphates are ignited with carbon; they are also formed in large quantity during the incineration of organic substances containing nitrates, or salts of organic acids. Treatment of an ash with ammonium carbonate, and re-ignition, is sometimes employed with the view of converting caustic lime and magnesia into carbonates. Such treatment converts sulphides and cyanides into carbonates; sulphate of calcium is also partially converted into carbonate if only a small proportion of alkali carbonate is present. Treatment with carbonic acid water is more free from objection, but its action is slow.

The chlorides found in an ash may be below the truth from volatilisation of alkali chlorides, if too high a temperature has been employed; or from loss of hydrochloric acid due to the action of organic acids produced during the charring of the organic matter; or from a similar action of silica, or dibasic phosphates, at a high temperature.

Phosphoric acid may be lost if acid phosphates are heated to a high temperature with carbonaceous matter. The alkali metals are also liable under some circumstances to suffer loss by volatilisation.

The ash constituents are obtained with the smallest loss when the ignition is conducted at a low temperature, preferably in a muffle. In some cases an excess of lime or baryta must be added to prevent losses of phosphoric acid and chlorine; this treatment also prevents the fusion of the ash (Strecker, *A.* 73, 366).

1. Ash of Animals.—The proportion of ash in some of the principal parts and products of the animal body, and its percentage composition, are shown in the following table. The figures are taken from Wolff's *Aschen Analysen* (1880), with the exception of the analysis of bone ash, which is quoted from *C. J.* 24, 80. The bone-ash represents the mean composition of all the carcase bones of the 'fat ox' analysed at Rothamsted. In this analysis, alkalis, and sulphuric and carbonic acids, were not determined; the whole amount of these constituents was, however, but 4·5 p.c. The 'pure ash' in Wolff's Tables is exclusive of sand, charcoal, and carbonic acid.

ASH OF ANIMAL PARTS AND PRODUCTS.

	Number of Analyses	Pure ash in 100 dry substance	100 parts of pure ash contain								
			K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Blood, human	4	—	26·6	24·1	0·9	0·5	8·2	8·8	7·1	—	30·7
,, ox	7	3·77	7·6	45·0	1·1	0·6	9·4	5·3	3·1	0·8	34·4
,, calf	2	—	11·2	41·0	1·8	1·2	8·3	7·8	1·3	—	34·7
,, sheep	2	—	7·1	45·0	1·1	0·6	9·6	5·5	1·9	—	35·8
,, pig	3	4·29	23·3	29·4	1·3	1·4	8·9	12·2	1·0	—	28·5
,, horse	1	—	29·5	21·2	1·1	0·6	9·5	8·4	6·3	—	28·6
,, dog	8	—	37·1	39·9	1·0	1·1	9·0	12·6	3·3	—	32·0
Flesh of mammalia	8	4·32	7·0	10·1	2·4	3·2	0·4	41·2	1·0	0·7	4·7
,, fowls	2	—	30·9	18·7	3·3	4·2	—	36·4	—	—	8·1
,, marine fish	1	—	21·8	14·9	15·2	3·9	—	31·5	—	—	11·4
Meat extract	11	20·89	43·9	12·8	0·7	3·1	0·4	29·8	2·2	0·9	10·0
Meat flour	2	1·80	5·4	3·0	22·4	3·5	13·3	43·5	1·2	0·9	1·8
Bone of ox carcase	1	—	—	—	53·5	1·0	0·2	40·3	—	0·5	—
Wool, unwashed	3	8·33	79·4	4·3	2·4	0·6	0·7	1·0	4·7	2·9	4·5
,, washed	1	1·11	19·1	2·7	24·7	6·0	18·2	3·2	—	25·3	0·8
Colostrum, cow	1	1·18*	7·2	5·7	34·9	2·1	0·5	41·4	0·2	—	11·8
Milk, human	4	0·49*	33·8	9·1	16·7	2·2	0·2	22·7	1·0	—	18·4
,, cow	9	0·72*	24·1	6·1	23·2	2·6	0·4	28·0	1·3	—	13·5
,, ewe	2	0·73*	21·3	3·8	29·3	0·1	1·0	35·8	1·6	2·0	7·5
,, mare	1	0·37*	25·1	3·4	30·1	3·0	0·4	31·9	—	—	7·5
,, sow	1	1·05*	6·2	6·7	39·2	1·8	0·9	37·2	1·3	—	9·3
,, bitch	2	0·73*	11·9	5·8	33·7	1·6	0·1	37·2	—	—	13·1
Whey, cow	3	0·51*	30·8	13·8	19·3	0·4	0·6	17·1	2·7	—	15·8
Hen's egg, without shell	3	3·48	17·4	22·9	10·9	1·1	0·4	37·6	0·3	0·3	9·0
,, white	3	4·61	31·4	31·6	2·8	2·8	0·6	4·4	2·1	1·1	28·8
,, yolk	3	2·91	9·3	5·9	13·0	2·1	1·7	65·5	—	0·9	1·9

* These numbers represent per cent. of pure ash in fresh substance.

The amount of ash yielded by the entire bodies of the principal animals reared on the farm, and its composition, have been determined by Lawes and Gilbert (*T.* 1883. 865); they also separately analysed the ash of the carcase and offal parts. The percentage composition of the ash of the entire bodies of calf, ox, lamb, sheep,

Properties.—Slender needles, v. sl. sol. cold, m. sol. hot, alcohol.

Reactions.—1. Gives on *oxidation* benzoic acid and tri-phenyl-carbinol.—2. Heating with alcoholic KOH produces tri-phenyl-methane and benzoic acid (Zagumenny, *Bl.* [2] 31, 330). 3. Reduced by HI to *s*-tetra-phenyl-ethane (?).

BENZPINACONE $C_{26}H_{22}O_2$ *i.e.* $Ph_2C(OH).C(OH).Ph_2$. *Tetra-phenyl-ethylene glycol.* [168°]. S. (benzene) 3·8 at 80°; S. (HOAc) 8·7 at 118°; S. (95 p.c. alcohol) 2·5 at 80°.

Formation.—From benzophenone by reducing the alcoholic solution with Zn and H_2SO_4 (Linnemann, *A.* 133, 26) or a solution in acetic acid (10 pts.) diluted with water (2 pts.) with zinc (Zagumenny, *J. R.* 12, 426).

Properties.—Minute prisms, sl. sol. boiling alcohol, v. sol. ether. On fusion it splits up into benzhydrol and benzophenone (Thörner a. Zincke, *B.* 10, 1473).

Reactions.—1. *Chromic acid* oxidises it to benzophenone.—2. *Sodium-amalgam* reduces it to di-phenyl-carbinol.—3. Readily converted into (α) or (β) benzpinacoline by dehydration; this is effected by BzCl, AcCl, dilute acids, or even by recrystallisation from alcohol (Za.).—4. Ac_2O gives benzhydrol and benzophenone.—5. HI and P at 170° give tetra-phenyl-ethane (Graebe, *B.* 8, 1054).

BENZ-URAMIDOXIM $C_8H_9N_3$ *i.e.* $C_6H_5.C(NOH)(NH.CO.NH_2)$. [115°]. Formed by the action of potassium cyanate upon benzamidoxim hydrochloride in conc. aqueous solution (Falck, *B.* 19, 1486). Long thin white needles. V. sol. alcohol, ether, benzene, and ligroïn, sl. sol. water.

BENZ-URANILIDOXIM $C_{14}H_{13}N_3O_2$ *i.e.* $C_6H_5.C(NOH).NPh.CO.NH_2$ (?). *Benz-phenyl-uramidoxim.* [167°]. Formed by the action of potassium cyanate upon benzanilidoxim hydrochloride in concentrated aqueous solution (Müller, *B.* 19, 1671). Yellowish needles. Sol. alcohol, ether, benzene, and chloroform, insol. water.

BENZYL. The radicle phenyl-methyl, $C_6H_5.CH_2$. It is isomeric with methyl-phenyl or tolyl $CH_3.C_6H_4$.

DIBENZYL *v.* *s*-DI-PHENYL-ETHANE.

BENZYL-ACETAMIDE *v.* *Acetyl*-BENZYL-AMINE.

BENZYL ACETATE $C_6H_5.CH_2.O.CO.CH_3$. (206°). S.G. $\frac{16\cdot5}{}$ 1·057. From benzyl alcohol (2 vols.), acetic acid (4 vols.) and H_2SO_4 (1 vol.), or by boiling benzyl chloride with alcoholic KOAc (Cannizzaro, *A.* 88, 130). Formed also by boiling a mixture of benzoic aldehyde and glacial acetic acid with zinc-dust (Tiemann, *B.* 19, 355). Oil, smelling of pears. *Sodium* acting upon benzyl acetate does not form benzyl aceto-acetate but the chief product is benzyl β-phenyl propionate: $4CH_3.CO_2C_7H_7 + Na_2 = 2CH_3CO_2Na + 2C_6H_5.CH_2.CO_2C_7H_7 + H_2$, and by a secondary reaction, sodic phenyl-propionate, sodic phenyl-acrylate, and toluene:

$$2C_6H_5.CH_2.CO_2C_7H_7 + Na_2 = C_6H_5CH_2.CO_2Na + C_6H_5.CH:CH.CO_2Na + 2C_6H_5CH_3$$

(Conrad a. Hodgkinson, *A.* 193, 300).

BENZYL-ACETIC ACID *v.* β-PHENYL-PROPIONIC ACID.

Di-benzyl-acetic acid $C_{16}H_{16}O_2$ *i.e.* $(C_6H_5.CH_2)_2CH.CO_2H$. *Di-phenyl-isobutyric acid* [85°]. Obtained by saponifying the ether, by heating di-benzyl-malonic ether with alcoholic KOH (Lellmann a. Schleich, *B.* 20, 439), or by heating di-benzyl-malonic acid (Bischoff a. Siebert, *A.* 239, 101).

Properties.—Prisms (from ligroïn), sl. sol. cold water, v. sol. alcohol. Heated with soda-lime it gives di-benzyl-methane.

Salts.—AgA′: trimetric prisms, sol. boiling water (Michael a. Palmer, *Am.* 7, 70).—BaA′₂.—CaA′₂aq.

Ethyl ether EtA′. (above 300°). Formed, together with β-phenyl-propionic ether by heating acetic ether with benzyl chloride and sodium (Lydia Sesemann, *B.* 6, 1086; Merz a. Weith, *B.* 10, 759).

BENZYL-ACETO-ACETIC ETHER *v.* p. 24.

BENZYL-ACETONE $C_{10}H_{12}O$ *i.e.* $C_6H_5.CH_2.CH_2.CO.CH_3$. *Methyl phenylethyl ketone.* (236°). S.G. $\frac{22\cdot5}{15}$ ·989.

Formation.—1. By the dry-distillation of a mixture of calcium hydrocinnamate and calcium acetate; the yield is 33 p.c. (Jackson, *B.* 14, 890). 2. From benzyl-aceto-acetic ether by boiling with alcoholic KOH (Ehrlich, *A.* 187, 15).

Properties.—Oil. Combines with $NaHSO_3$ forming $C_{10}H_{12}ONaHSO_3aq$. Oxidised by CrO_3 to acetic and benzoic acids.

BENZYL-ACETONE γ-CARBOXYLIC ACID *v.* ACETYL-PHENYL-PROPIONIC ACID.

Benzyl-acetone *o*-carboxylic-acid $C_{11}H_{12}O_3$ *i.e.* $CO_2H.C_6H_4.CH_2.CH_2.CO.CH_3$. [114°]. Obtained by boiling *o*-carboxy-benzyl-aceto-acetic ether with baryta-water (Bülow, *A.* 236, 192). Slender needles (from water).

BENZYL-ACETOXIM *v.* ACETOXIM, p. 38.

BENZYL-ACETYL-SUCCINIC ETHER *v.* ACETYL-BENZYL-SUCCINIC ETHER, p. 39.

ν-**BENZYL-DI-ACETYL-PYRROL** *v.* BENZYL-PYRRYLENE-DI-METHYL-KETONE.

BENZYL ALCOHOL C_7H_8O *i.e.* $C_6H_5.CH_2.OH$ Mol. w. 108. (206·5°). S.G. $\frac{20}{4}$ 1·0429 (Brühl S. 4 at 17°. μ_β 1·5518. R_∞ 53·16. H.F. 38,73 (Stohmann, *J. pr.* [2] 36, 4).

Occurrence.—Balsam of Peru contains benzyl benzoate, benzyl cinnamate and small quantities of benzyl alcohol (Kraut, *A.* 152, 129). Liquid storax contains benzyl cinnamate (Laubenheimer, *A.* 164, 289). Balsam of tolu contains benzyl cinnamate and some benzyl benzoate (Busse, *B.* 9, 830). In small quantity, together with benzoic aldehyde, prussic acid, and a resin in the volatile oil of cherry-laurel (Tilden, *Ph.* [3] 5, 761).

Formation.—1. Together with KOBz by the action of alcoholic KOH on benzoic aldehyde (Cannizzaro, *A.* 88, 129). 2. From benzyl chloride by converting it into benzyl acetate by alcoholic KOAc, and boiling the product with alcoholic KOH (Cannizzaro, *A.* 96, 246).—3. From benzyl chloride by heating with an aqueous solution of K_2CO_3 (Meunier, *Bl.* [2] 38, 159); with water (10 pts.) and freshly ppd. $Pb(OH)_2$ (3 pts.) (Lauth a. Grimaux, *A.* 143, 81); or merely with water (30 pts.) (Niederist, *A.* 196, 353).—4. From balsam of Peru by boiling with aqueous KOH (Kachler, *J. pr.* 107, 807).—5. By the action of sodium-amalgam upon

benzoic aldehyde (Friedel, *J.* 1862, 263), benzoic acid, hippuric acid (Hermann, *A.* 132, 76; 133, 335), benzoyl chloride in presence of HCl (Lippmann, *Bl.* [2] 4, 249), or benzamide (Guareschi, *G.* 4, 465).

Preparation.—10 pts. of benzaldehyde are shaken in a stoppered cylinder with a solution of 9 pts. of KOH in 6 pts. of water, and left to stand over-night. Sufficient water is then added to dissolve the potassium benzoate which has separated, and the solution is extracted with ether; after evaporating the ether the residue is distilled; the yield is 92 p.c. of the theoretical. Benzyl alcohol cannot be dried with $CaCl_2$ as it combines with it (Meyer, *B.* 14, 2394).

Properties.—Liquid with little odour, sl. sol. water, sol. alcohol and ether.

Reactions.—1. Oxidised by dilute HNO_3 or air and platinum black to benzoic aldehyde, and by CrO_3 to benzoic acid.—2. HI and P at 140° reduce it to toluene (Graebe, *B.* 8, 1054).—3. Alcoholic KOH forms toluene and benzoic acid (Cannizzaro, *A.* 90, 253).—4. Conc. H_2SO_4, P_2O_5, and $ZnCl_2$ form a resin (Cannizzaro, *A.* 92, 113).—5. B_2O_3 at 110° forms di-benzyl oxide $(C_6H_5.CH_2)_2O$.—6. Solid *cyanogen chloride* forms benzyl carbamate and di-benzyl-urea (Cannizzaro, *G.* 1, 33; *B.* 3, 517). 7. *Urea nitrate* at 120° forms di-benzyl-urea and benzoic aldehyde; at 140° it forms benzyl carbamate (Campisi a. Amato, *G.* 1, 39).—8. BCl_3 forms *s*-di-phenyl-ethane and benzyl chloride (Councler, *B.* 10, 1655).

Methyl ether $C_6H_5.CH_2.OMe$. (168°). From benzyl chloride, KOH, and MeOH (Sintenis, *A.* 161, 334). Also from benzyl sulphide, methyl alcohol, and MeI (Cahours, *A. Ch.* [5] 10, 23).

Ethyl ether $C_6H_5.CH_2.OEt$. (185°). Gives anthracene when heated with P_2O_5. Chlorine in the cold forms HCl, ethyl chloride, and C_6H_5CHO; at a higher temperature it gives EtCl and benzyl chloride. Chlorine in the cold in presence of I forms chloro-benzoic aldehydes and EtI (Sintenis, *A.* 161, 331). Br forms in the cold HBr, EtBr, benzyl bromide, benzoic aldehyde, and BzBr (Paternò, *B.* 5, 288).

Isobutyl ether $C_6H_5.CH_2.O.C_4H_9$. (c. 210°) (Claus a. Trainer, *B.* 19, 3006).

Phenyl ether $PhO.CH_2Ph$. [39°]. (287°). From phenol-potassium, benzyl chloride and a little alcohol at 100° with inverted condenser for 3 hours (Staedel, *A.* 217, 44; Lauth a. Grimaux, *A.* 143, 81; Sintenis, *A.* 161, 337). Glittering white plates which feel greasy (from alcohol). Conc. HCl at 100° splits it up into phenol and benzyl chloride. Chlorine in presence of HgO forms the chloro-phenyl ether, $C_6H_5.CH_2.O.C_6H_4Cl$ [71°]; bromine forms similarly $C_6H_5.CH_2.O.C_6H_4Br$ [60°].

o-Tolyl ether $C_6H_5.CH_2.O.C_6H_4.CH_3$ [1:2]. *Benzyl o-cresyl oxide.* (285°–290°) (Staedel, *B.* 14, 899).

m-Tolyl ether $C_6H_5.CH_2.O.C_6H_4.CH_3$ [1:3]. [43°]. (300°–305°). Satiny tablets.

p-Tolyl ether $C_6H_5.CH_2.O.C_6H_4.CH_3$ [1:4]. [41°]. From potassium *p*-cresol, a little alcohol, and benzyl chloride (Staedel, *A.* 217, 44). The yield is 86 p.c. White silky scales or transparent six-sided columns (from alcohol). Feels greasy.

(α)-*Naphthyl ether.* An oil, decomposed by distillation.

(β)-*Naphthyl ether* $C_{10}H_7O.CH_2Ph$. [99°]. From (β)-naphthol (70 g.), KOH (27 g.), a little water and alcohol, and benzyl chloride (70 g.). White plates (from alcohol). No smell. Not volatile with steam (Staedel, *A.* 217, 47).

Other benzyl ethers are described under the hydroxylated compounds from which they are derived.

BENZYL-o-AMIDO-ACETOPHENONE

$C_6H_4(NHC_7H_7).CO.CH_3$. [81°]. Formed by heating *o*-amido-acetophenone with benzyl chloride (Baeyer, *B.* 17, 971). Large prisms. V. sol. alcohol, ether, benzene, chloroform and CS_2, sl. sol. ligroïn. Weak base.

Nitrosamine $C_6H_4(N(C_7H_7).NO)CO.CH_3$ [55°]; long colourless needles. By heating with H_2SO_4 it gives a mixture of indigo and benzyl-indigo.

BENZYL-o-AMIDO-BENZOIC ACID

$C_7H_7NH.C_6H_4.CO_2H$. [176° uncor.]. Formed together with its formyl derivative by oxidation of benzyl-quinoline with alkaline $KMnO_4$. Long needles or thick prisms.

Salts $C_{14}H_{13}NO_2HCl$: [105° uncor.]; large tables.—$(C_{14}H_{13}NO_2)_2H_2Cl_2PtCl_4$: [158° uncor.]; orange yellow tables.

Formyl derivative $C_7H_7N(CHO).C_6H_4.CO_2H$ [196°]; large colourless tables (Claus a. Glyckherr, *B.* 16, 1283).

BENZYL-AMIDO-TRI-PHENYL-METHANE

$Ph_3C.NH.CH_2Ph$. [110°]. The hydrochloride B'HCl [249°] is formed by the action of benzyl chloride on ω-amido-tri-phenyl-methane (Elbs, *B.* 17, 703).

Di-benzyl-amido-di-phenyl-methane

$Ph.CH_2.C_6H_4N(CH_2Ph)_2$. From aniline hydrochloride and benzyl chloride at 120°. Also from acetanilide and benzyl chloride at 120°. White amorphous powder (Meldola, *C. J.* 41, 200). Soluble in benzene. Solutions have a blue fluorescence.

BENZYLAMINE C_7H_9N *i.e.* $C_6H_5.CH_2.NH_2$. Mol. w. 107. (184°). S.G. $\frac{14}{}$ ·99.

Formation.—1. Together with di- and tri-benzylamine by heating benzyl chloride with alcoholic NH_3 (Cannizzaro, *A.* 134, 128; Limpricht, *A.* 144, 304).—2. Together with di- and tri-benzylamine by the action of Zn and HCl upon benzonitrile (Mendius, *A.* 121, 144; Spica, *G.* 10, 515).—3. By reducing thiobenzamide $C_6H_5.CSNH_2$ with Zn and HCl (Hofmann, *B.* 1, 102).—4. From benzyl cyanate and KOH (Strakosch, *B.* 5, 692).—5. By saponification of its acetyl derivative, obtained by the action of acetamide on benzyl chloride (Rudolph, *B.* 12, 1297).—6. By the action of bromine in alkaline solution on phenyl-acet-amide $C_6H_5.CH_2.CONH_2$: the yield is 60 p.c. of the theoretical quantity (Hofmann, *B.* 18, 2738; Hoogewerff a. Van Dorp, *R. T. C.* 5, 252).—7. Together with toluene, by energetic reduction of hydrobenzamide dissolved in absolute alcohol by means of sodium or sodium-amalgam; very good yield (O. Fischer, *B.* 19, 748).—8. By reduction of an alcoholic solution of benzaldehyde-phenyl-hydrazide by means of sodium-amalgam and acetic acid (Tafel, *B.* 19, 1928).—9. By reduction of benzaldoxim (5 pts.), dissolved in alcohol (15 pts.), at 50°–60° with sodium-amalgam (160 pts. of 2½ p.c. Na), keeping acid by gradual addition of acetic acid: good yield (Goldschmidt,

and pig will be found below. The composition in 1,000 parts of the fasted live weight of the animal body is also given. The latter will afford data for calculating the loss which a farm suffers by sale of stock. The fasted live-weight is inclusive of contents of stomach and intestines, but the constituents of these contents are not reckoned among the animal constituents. The 'pure ash' is inclusive of carbonic acid.

2. Ash of Plants. The composition of the ash of plants of agricultural importance will be given under the headings of the different crops, some general considerations will, however, be best made in the present place.

Percentage Composition of Ash from entire Bodies of Animals.

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl	CO_2
Fat calf . . .	5·4	3·8	44·0	2·2	0·5	40·4	1·1	0·1	1·6	1·3
Half-fat ox . . .	4·4	3·1	45·3	2·0	1·0	40·2	0·9	0·2	1·2	2·0
Fat ox . . .	4·5	3·0	46·6	1·5	0·4	39·8	0·8	0·1	1·5	2·1
Fat lamb . . .	5·7	3·6	41·6	1·8	0·6	39·0	1·2	0·3	1·9	1·5
Store sheep . . .	5·6	3·9	43·1	1·8	1·2	39·0	1·8	0·7	2·3	1·1
Half-fat old sheep .	5·3	3·4	44·4	1·7	1·4	39·2	1·1	0·6	1·6	1·8
Fat sheep . . .	5·5	3·6	44·6	1·8	1·0	38·7	1·0	0·9	1·6	1·7
Very fat sheep . .	5·5	4·5	43·3	1·9	1·0	38·7	1·0	0·6	2·3	1·7
Store pig . . .	7·1	4·2	40·6	2·0	0·9	40·1	2·3	0·2	2·2	0·6
Fat pig . . .	8·6	4·4	38·5	2·0	0·8	40·1	2·2	0·1	2·8	1·2

Composition of Animal Bodies, per 1,000 parts fasted live weight.

	Fat Calf.	Half-fat Ox.	Fat Ox.	Fat Lamb.	Store Sheep.	Half-fat old Sheep.	Fat Sheep.	Very fat Sheep.	Store Pig.	Fat Pig.
Contents of stomach and intestines, moist	32·0	82·0	60·0	85·0	60·0	91·0	60·0	52·0	52·0	40·0
Water	630·0	515·0	455·0	478·0	573·0	502·0	434·0	352·0	551·0	413·0
Fat	118·0	191·0	301·0	285·0	187·0	235·0	356·0	458·0	233·0	422·0
Nitrogenous substance	152·0	166·0	145·0	123·0	148·0	140·0	122·0	109·0	137·0	109·0
Crude ash . . .	38·0	46·6	39·2	29·4	31·6	31·7	28·1	29·0	26·7	16·5
Pure ash . . .	37·8	46·1	38·8	28·9	30·6	30·6	26·8	28·6	26·5	16·3
K_2O	2·06	2·05	1·76	1·66	1·74	1·68	1·48	1·58	1·96	1·38
Na_2O	1·48	1·46	1·26	1·03	1·20	1·04	0·97	1·29	1·10	0·73
CaO	16·46	21·11	17·92	12·81	13·21	13·50	11·84	12·40	10·79	6·36
MgO	0·79	0·85	0·61	0·52	0·56	0·52	0·18	0·55	0·53	0·32
Fe_2O_3	0·21	0·41	0·24	0·26	0·37	0·42	0·34	0·30	0·22	0·13
P_2O_5	15·35	18·39	15·51	11·26	11·88	11·99	10·40	11·08	10·66	6·54
SO_3	0·41	0·38	0·33	0·39	0·52	0·35	0·31	0·29	0·53	0·29
SiO_2	0·05	0·13	0·06	0·12	0·21	0·20	0·26	0·16	0·05	0·03
Cl	0·63	0·59	0·55	0·53	0·72	0·51	0·44	0·66	0·57	0·43
CO_2	0·47	0·87	0·71	0·43	0·37	0·53	0·41	0·19	0·21	0·21

The ash constituents of a plant are obtained from the soil by the roots. All matters in the soil which are soluble and diffusible will enter the plant by the root, the abundant evaporation of water from the surface of a growing plant maintaining a rise of liquid in the capillary vessels. The substances entering the plant are not, however, limited to those existing in solution in the soil, as the roots of plants exercise a solvent or digestive action on constituents of the soil not otherwise soluble in water. The wide differences in the assimilating powers of the roots of different plants are well illustrated by the special assimilation of alumina by the *Lycopodiaceæ*, and of silica by the *Equisetaceæ* and *Graminaceæ*.

The ash constituents which enter the circulation of the plant are (1) partly employed in the formation of new tissue; (2) partly deposited as incrusting matter on the older tissues; while (3) soluble salts that are of no advantage to the plant first accumulate in the sap, and then are gradually removed from the plant by the action of rain, and possibly by diffusion into the soil through the roots. The ash constituents most largely consumed in the formation of tissue are potash and phosphoric acid; in all the actively growing parts of a plant potash and phosphoric acid greatly preponderate. Magnesia, lime, oxide of iron, and sulphuric acid, must also be reckoned as essential for plant growth. The incrusting ash constituents are calcium salts and silica; these are chiefly precipitated in the leaves, where evaporation is most active. The soluble salts remaining unused in the sap generally contain a large proportion of chlorides, and of sodium salts.

A vigorous plant will take from a rich soil a much larger quantity of ash constituents, especially of alkali salts, than is necessary for its growth. For the same reason a plant growing on different soils may yield a very different ash. Thus a clover or bean plant will be rich in

potash or lime according as one or the other preponderates in the soil. On the other hand plants clearly exercise a selective power, potash being stored up in large quantity, though soda rather than potash may be abundant in the soil. This selective power is apparently not a property of the roots, but simply results from the fact that potash is removed from the sap to form tissue, while soda is not; potash salts can thus continue to enter the roots by diffusion or otherwise, while sodium salts having accumulated in the sap the tendency of diffusion is now for them to pass through the roots into the moist soil (see Dehérain, *Cours de Chimie agricole* [1873] 77). The Rothamsted experiments show that potash greatly preponderates in hay, and in barley straw, when the soil supplies a sufficient quantity; but when potash fails, soda is retained by the plant to a considerable extent.

The variations in the composition of the ash of any plant do not extend to the seed; the ash of this is of very definite composition whatever the nature of the soil. The ash of a seed consists chiefly of potassium phosphate; soda is practically absent.

While the seed is forming, a migration of phosphoric acid and potash, and of nitrogenous matter and carbohydrates, sets in from all parts of the plant, the roots included; a great part of these important constituents is finally stored in the seed. The extent to which the exhaustion of the plant, and the enrichment of the seed, proceeds, depends on the climate during the ripening period. R. W.

ASPARAGINE

$C_4H_8N_2O_3$ *i.e.* $CO_2H.CH_2.CH(NH_2).CO.NH_2$ or $CONH_2.CH_2CH(NH_2).CO_2H$. *Amido-succinamic acid.* M. w. 150 (containing aq) S.G. $\frac{14}{}$ 1·52. S. c. 1·8 at 10·5°; 53 at 100°. Occurs in juice of most plants, especially in growing buds and germinating seeds (*e.g.* asparagus, marsh-mallow, comfrey, potatoes, deadly nightshade, chestnuts, liquorice root, lettuce, convolvulus root, dahlia tubers, young shoots of vetch, peas, beans, and other leguminous plants). Lupine seeds that have not begun to grow contain no asparagine; after 15 days' germination more than 20 p.c. of asparagine may be extracted by water (Schulze a. Barbieri, *J. pr.* [2] 27, 339). When twigs full of young leaf-buds of the plane, birch, or horse-chestnut are cut off and allowed to open by placing the cut end in water, the leaves are found to contain asparagine (S. a. B., *J. pr.* 133, 145). Asparagine may be formed by adding conc. ammonia to mono-ethyl aspartate (Schaal, *A.* 157, 24).

Properties.—Trimetric prisms (containing aq) exhibiting left-handed hemihedry. Sol. water, acids, and alkalis; insol. alcohol and ether. Its solution in water or alkalis is lævorotatory, in acids it is dextrorotatory. In HCl solution $[\alpha]_D$ = about + 36°; in aqueous solution about −6°; in ammoniacal solution about −11°.

Reactions.—1. Boiling with *lime*, or *baryta-water*, or with dilute H_2SO_4 rapidly converts it into aspartic acid.—2. *Nitrous acid* forms malic acid.—3. Impure asparagine is liable to undergo *fermentation*, changing to ammonic succinate. 4. MeI and KOH produce an amide of fumaric acid, $CO_2H.CH:CH.CONH_2$ (Michael a. Wing, *Am.* 6, 419; Griess, *B.* 12, 2117).

Salts.—$HA'HCl$. — $(HA')_2HCl$. — CuA'_2. — CaA'_2. — ZnA'_2. — $HA'HgCl_2$. — AgA'. — $HA'(AgNO_3)_2$. — $HA'C_6H_2(NO_2)_3OH$: yellow prisms (Smolka, *M.* 6, 915).

Estimation.—Heat the extract containing it with dilute HCl for some hours and determine the amount of NH_4Cl formed. This corresponds to half the nitrogen in asparagine (Sachsse, *J. pr.* [2] 6, 118). Glutamine also splits off half its amidogen as ammonia when treated with HCl. Or the extract may be treated with bromine and NaOH (measuring evolved N_2) both before and after heating with HCl (Sachsse). But asparagine gives off too much N_2 when so treated (Morgen, *Fr.* 20, 37). It even gives off a little N_2 when treated with NaBrO before heating with HCl. These two errors nearly balance one another (E. Schulze, *J. pr.* [2] 31, 235). Solutions of sodic aspartate give off no N_2 with NaBrO, but if NH_3 be present more N_2 is evolved than corresponds to the NH_3. The increase may be 6 p.c. Leucine behaves in the same way as asparagine, but tyrosine behaves in exactly the opposite manner. Urea has the same influence as NH_3. It is therefore better to determine the free NH_3 by distilling with MgO, CaO or even NaOH (comp. Berthelot a. André, *C. R.* 103, 1051). The presence of peptones will, of course, invalidate the determination, these are often absent from vegetable solutions; if present they must be removed: albuminoids may be ppd. by lead salts, peptones by tannin or phosphotungstic acid (E. Schultze, *l.c.*).

Dextro-asparagine

$C_2H_3(NH_2)(CO_2H).CO.NH_2$. Dextro-hemihedral crystals. Dextrorotatory $[\alpha]_D$ = + 5°41′. Very sweet taste (ordinary asparagine is tasteless). Rather more soluble in water than ordinary asparagine. Occurs in the mother-liquors obtained in re-crystallising the crude asparagine prepared from the shoots of the vetch; 20 kilos of crude asparagine, obtained from 6500 kilos. of vetch gave 100 grms. of the pure dextro-asparagine.

The compounds prepared from dextro-asparagine exhibit the same properties as those prepared from the lævo-asparagine except that their rotatory power is reversed. By heating with 2 mols. of aqueous HCl at 170°–180° both asparagines give the same inactive aspartic acid (Piutti, *C. R.* 103, 134; *B.* 19, 1691).

Additional References.—Vauquelin a. Robiquet, *A. Ch.* 57, 88; Dessaignes, *A.* 82, 237; Piria, *A. Ch.* [3] 22, 160; Pasteur, *A. Ch.* [3] 31, 70; Mercadante, *G.* 5, 187; Portes, *B.* 9, 1934; Dubrunfaut, *J. pr.* 53, 508; Gorup-Besanez, *A.* 125, 291; Champion a. Pellet, *B.* 9, 724; Becker, *B.* 14, 1031; De Luca a. Ubaldini, *C. R.* 59, 527; Buchner, *Z.* 1862, 117; Campani, *Z.* [2] 6, 87; E. Schulze, *B.* 15, 2855; *J. pr.* [2] 20, 397; 27, 339.

ASPARTIC ACID $C_4H_7NO_4$ *i.e.* $CO_2H.CH_2.CH(NH_2).CO_2H$. *Amido-succinic acid.* Mol. w. 133. S.G. $\frac{12.5}{}$ 1·66. S. ·45 at 20°; 5·4 100°.

Formation.—1. By boiling asparagine with lime, baryta, PbO, KOH, or HCl dissolved in water.—2. By boiling albumen or caseïn with dilute H_2SO_4 (Kreussler, *J. pr.* 107, 239; Ritthausen, *J. pr.* 107, 218).—3. By treating proteïds with bromine (Hlasiwetz a. Habermann, *A.* 159, 325).—4. From caseïn by treatment

with $SnCl_2$ and HCl (H. a. H., *A.* 169, 162).—5. From diazo-succinic ether by reduction with zinc dust and acetic acid (Curtius a. Koch, *B.* 19, 2460).

Preparation: 100 grms. of asparagine are boiled for 2 or 3 hours with an inverted condenser with 408 c.c. of pure aqueous hydric chloride (containing ·11925 g. HCl per c.c.). To the cooled solution is then added 204 c.c. of aqueous NH_3 (corresponding to the acid volume for volume). On standing for several hours the aspartic acid separates in colourless crystals. The yield is 90 p.c. of the theoretical (Schiff, *B.* 17, 2929).

Properties.—Small trimetric rectangular plates. Sl. sol. water, insol. alcohol. Its solutions in alkalis are lævorotatory; its solution in HClAq is dextrorotatory, $[\alpha]_D = +28°$. The rotation is affected by the nature of the solution (Becker, *B.* 14, 1035). Aspartic acid (1 mol.) prevents the ppn. of $Cu(OH)_2$ (1 mol.) by KOH.

Reactions.—1. *Nitrous acid* converts it into malic acid.—2. MeI and KOH form fumaric acid (Korner a. Menozzi, *R. Istit. Lombard.* 13, 352).—3. Not affected by *boiling water* or by *magnesia*.—4. Heating in a current of HCl at 130°-200° produces two anhydrides: (*a*) insoluble in water ($C_{32}H_{26}N_8O_{17}$), (*b*) slightly soluble in water ($C_{16}H_{14}N_4O_9$). Both are converted by boiling baryta into aspartic acid; but when the former is heated for 2 hours at 125° with half its weight of urea it produces a gummy mass, soluble in water forming a solution that has all the characters of a proteïd. It is ppd. by acids, by NaCl, $MgSO_4$, tannin, and $HgCl_2$ forming gelatinous pps. $CuSO_4$ and KOH give a violet solution (Grimaux, *C. R.* 93, 771).

S a l t s.—$H_2A''HCl$: deliquescent crystals.—$H_2A''H_2SO_4$.—$NaHA''$ aq: trimetric prisms; S. 89 at 12°.—$BaH_2A''_2$ 4aq.—BaA''3aq.—CaA''4aq — HgA''. — $PbH_2A''_2$. — PbA''. — $AgHA''$. — Ag_2A''.—CuA'' 4½aq. S. ·035 at 15°; ·43 at 100°; v. sol. dilute HOAc. The insolubility of this salt may be used to detect and to isolate aspartic acid (Hoffmeister, *Sitz. B.* 75, 469).—CuA''3aq (Curtius a. Koch, *B.* 19, 2460).

Mono-ethyl ether $A''EtH$. Its hydrochloride $(A''HEt)_2HCl$ forms large colourless needles, [199°].

Di-ethyl ether $A''Et_2$. Its hydrochloride $A''Et_2$,HCl forms excessively hygroscopic concentric needles.

Di-methyl ether $A''Me_2$. Its hydrochloride $A''Me_2$,HCl forms very hygroscopic glistening prisms (Curtius a. Koch, *B.* 18, 1293).

Amide v. ASPARAGINE.

Di-phenyl-amide
$CO_2H.C_2H_3NH_2.CONPh_2$. [230°]. Formed, together with phthalimide, by the action of NH_3 on the diphenylamide of phthalyl-amido-succinic acid $CO_2H.C_2H_3N(C_2O_2C_6H_4).CONPh_2$ (Piutti, *G.* 16, 14).

Inactive aspartic acid $C_4H_7NO_4$. S. ·42 at 7°.

Formation.—1. By the action of boiling HCl on the product obtained by heating the acid ammonium salts of malic, maleïc or fumaric acid.—2. By heating an aqueous solution of the hydrochloride of active aspartic acid for several hours at 170° (Michael a. Wing, *B.* 17, 2984; *Am.* 7, 278).

Properties.—Monoclinic needles. Converted by nitrous acid into inactive malic acid.

Salts.—PbA''.—Ag_2A''.—$H_2A''HCl$.

Lævo-aspartic acid $C_4H_7NO_4$. **Obtained from dextro-asparagine by treatment with HCl (Piutti, *B.* 19, 1693). Lævorotatory. Its properties are the same as those of the dextrorotatory acid. Combines with dextro-acid to form an inactive modification.**

Additional References.—Plisson, *A. Ch.* 40, 303; 45, 315; Boutron-Chautard a. Pelouze, *A. Ch.* 52, 90; Liebig, *P.* 31, 232; *A.* 26, 125, 161; Wolff, *A.* 75, 293; Piria, *A. Ch.* [3] 22, 160; Dessaignes, *C. R.* 30, 324; 31, 432; *A.* 83, 83; *J. Ph.* [3] 32, 49; Pasteur, *A. Ch.* [3] 34, 30; *A.* 82, 324; Pott, *J. pr.* [2] 6, 91; Radziszewski a. Salkowski, *B.* 7, 1050; Ritthausen a. Kreussler, *J. pr.* [2] 3, 314; Scheibler, *J. Ph.* [4] 4, 152; *B.* 2, 296; Kreussler, *Z.* [2] 6, 93.

ASPHALT. A natural product of the decomposition of vegetable substances. It is found on the shores of the Dead Sea, also in a molten state in Trinidad, and as a mineral deposit at Seyssel. It frequently impregnates other rocks. When distilled with water, *petrolene* $C_{20}H_{32}$ (280°), S.G. $\frac{21}{}$ ·89, V.D. 9·5, passes over (Boussingault, *A. Ch.* [2] 64, 141; Voelckel, *A.* 87, 139).

ASPIDOSAMINE $C_{22}H_{28}N_2O_2$. [c. 100°]. In quebracho bark (Hesse, *A.* 211, 263). Turns yellow in air. V. e. sol. ether, chloroform, benzene or alcohol, v. sl. sol. light petroleum, insol. water. Its alcoholic solution turns litmus blue, neutralises HCl and tastes bitter.

Reactions.—1. Solution of hydrochloride gives with Fe_2Cl_6 a brownish-red colour.—2. Conc. H_2SO_4 gives a bluish solution.—3. Conc. H_2SO_4 and MoO_3 gives a blue liquid.—4. Conc. H_2SO_4 and $K_2Cr_2O_7$ gives a dark blue colour.—5. Boiling aqueous $HClO_4$ gives a magenta colour.

Platinochloride. $B'_2H_2PtCl_6$ 3aq.

ASPIDOSPERMATINE $C_{22}H_{28}N_2O_2$. [162°]. In quebracho bark (Hesse, *A.* 211, 259). Crystalline. V. sol. chloroform, alcohol, or ether. In alcohol (97 p.c.) it turns litmus blue, has a bitter taste, and is lævorotatory $[\alpha]_D = -72·3°$ at 15° in a 2 p.c. solution.

Reactions.—1. $HClO_4$ gives a magenta colour. 2. Conc. H_2SO_4 and $K_2Cr_2O_7$ give no colour.—3. Fe_2Cl_6 gives no colour.

S a l t s.—Dilute HCl is neutralised by aspidospermatine. NaOH or NH_3 give in the solution a flocculent pp. (m. sol. pure water) which soon becomes crystalline. Salts are amorphous.—$(B'HCl)_2PtCl_4$ 4aq.

ASPIDOSPERMINE $C_{22}H_{30}N_2O_2$. [206°] $[\alpha]_D$ (alcohol) $-100·2°$; (chloroform) $-83·6°$; (dilute HCl) $-62°$ (in all cases 2 p.c. solution at 15°). S. (alcohol) 2 at 14°; (ether) ·74 at 14° (Wulfsberg, *Ph.* [3] 11, 269). An alkaloid present (with others) in bark called in the Argentine Republic quebracho blanco or quebracho colorado (Fraude, *B.* 11, 2189; Hesse, *A.* 211, 251; Arata, *C. J.* 40, 622). Needles or pointed prisms (from alcohol or light petroleum). M. sol. alcohol, sl. sol. ether or light petroleum, v. sol. benzene or chloroform. Lævorotatory.

Reactions.—1. HCl and $PtCl_4$ give a blue pp.—2. $HClO_4$ gives a magenta colour.—3. Conc. H_2SO_4 no colour.—4. Conc. H_2SO_4 and MoO_3 no colour.—5. Conc. H_2SO_4 and $K_2Cr_2O_7$, a brownish-red turning dark green.—6. Salts give with

NH_3, NaOH, Na_2CO_3, or $NaHCO_3$, a white flocculent pp. becoming crystalline.

Salts.—Very unstable; even ether or $CHCl_3$ can partly decompose them.—$B'_2H_2PtCl_6$ 4aq.

ASSAMAR. A name given by Reichenbach (*A.* 49, 3) to a bitter, deliquescent, transparent yellow solid which may be extracted by alcohol from toasted bread. It is insol. ether. The same name was given by Völckel (*A.* 85, 74) to a thick yellow neutral syrup obtained from the aqueous portion of the product of the distillation of cane-sugar. It is sol. ether. Both substances reduce aqueous $AgNO_3$.

ASYMMETRIC CARBON. A name applied to an atom of carbon that is united to four different atoms or radicles. All compounds that in the liquid state or in solution rotate light contain asymmetric carbon (Van 't Hoff, *La chimie dans l'espace*; Le Bel, *Bl.* [2] 22, 337).

ATHAMANTA, OIL OF. $C_{10}H_{16}$. (163°). S.G. ·84. An essential oil obtained from the leaves of *Athamanta oreoselinum.* It forms a liquid compound with HCl (190°) (Schnedermann a. Winckler, *A.* 51, 336).

ATHAMANTIN $C_{24}H_{30}O_7$. [79°]. In the root and seeds of *Athamanta oreoselinum.* Fibrous, silky crystals, or sometimes rectangular prisms; insol. water, v. sol. alcohol and ether. It gives valeric acid on dry distillation. Aqueous acids and alkalis split it up into valeric acid and oreoselone $C_{14}H_{12}O_4$. Chloro-, and tri-nitro-, athamantin are amorphous (Schnedermann, *A.* 51, 315; Geyger, *A.* 110, 359).

ATHEROSPERMINE [128°]. An alkaloid in the bark of *Atherosperma moschatum.* A greyish-white powder with bitter taste. V. sl. sol. water, m. sol. alcohol, sl. sol. ether. The solution of its hydrochloride gives pps. with phosphomolybdic acid, picric acid, tannin, and $PtCl_4$. It liberates iodine from iodic acid (Zeyer, *J.* 1861, 769).

ATMOSPHERE. The word *Atmosphere* (ἀτμός, vapour; σφαῖρα, a globe) in its most extended sense signifies the gaseous envelope which surrounds any liquid or solid body: more commonly, however, it is taken to mean the invisible elastic fluid which surrounds the earth. A variety of phenomena, *e.g.* solar and terrestrial radiation, animal and vegetable life, weather, the disintegration of rocks and the formation of soils, the propagation of sound, &c., are dependent on the existence of a terrestrial atmosphere. The earth is not the only planetary body which possesses an atmosphere. The Sun, Jupiter, Mars, Saturn, have doubtless very dense atmospheres, but as yet we have no exact knowledge of their physical and chemical natures.

The phenomena of solar eclipses, and the facts that a single star seems to disappear instantly when it is occulted opposite the smooth part of the moon's limb, and that there is no change of colour or other effect such as a refractive atmosphere would occasion, make it certain that the moon's atmosphere, if it exists at all, must be of extreme tenuity. This conclusion is strengthened by evidence afforded by the spectroscope. It has been observed that the spectrum of the moon's light is identical with the solar spectrum and there is no trace of any absorptive action; moreover, it is found that the spectrum of a star during its occultation disappears as suddenly as the star itself.

Wollaston's arguments as to the finite extent of the terrestrial atmosphere were deemed inconclusive even by his contemporaries. There is indeed direct evidence for the belief that air is present in a state of sensible density at much greater heights than 40 or 45 miles which was the limit Wollaston assigned. Liais, from observations on the phenomena of sunlight at Rio Janeiro, arrived at a superior limit of 200 miles; and Secchi, from observations on luminous meteors, calculated that air exists of appreciable density even at a height of 200 kilometres above the earth's surface. It is in fact probable that no actual limit exists. Up to the present it has been impossible to arrive at direct results otherwise than by astronomical observations, as the law of the diminution of temperature which in great measure governs the extent of the repulsion among gaseous particles is unknown for the upper strata of the atmosphere. No arguments can be based on the finite expansibility of gases. Faraday's experiments on the limits of vaporisation of mercury have been controverted by Merget. It is obvious that the relative distribution of the mass of the air will be modified by the increase of attraction at the poles as compared with that at the equator; by the increase of temperature as we approach the torrid zone; and by the earth's motion.

The ponderability of air although suspected before the time of Aristotle was first conclusively demonstrated by Galileo, who found that a copper ball containing condensed air weighed more than when filled with air of ordinary tension. The weight of 1 litre of air, freed from aqueous vapour, carbonic acid, and ammonia, at 0°C., and under a pressure of 0·76 m. of mercury, at Paris (lat. 48° 50′), and at a height of 60 m. above the sea level, was found by Regnault to be 1·293187 grams. According to Regnault 1 litre of oxygen at the normal temperature and pressure weighs 1·429802 grams; 1 litre of nitrogen under the same conditions weighs 1·256167 grams. If x be the volume of oxygen contained in 1 litre of air, and $1-x$ that of the nitrogen, then $1·429802x + (1-x)\ 1·256167 = 1·293187$, whence $x = 0·2132$ or in per cents. 21·32, which is considerably higher than that found by eudiometric analysis. According to Magnus 1 litre of pure air at 0° and ·76 m. weighs at Berlin (lat. 52° 30′) 1·29306 grams. Ph. v. Jolly found that at Munich (lat. 48° 8′, 515 m. above the sea's level) 1 litre of oxygen at 0° and ·76 m. weighed 1·429094 grams; and 1 litre of nitrogen under the same conditions weighed 1·257614 grams. Reducing these numbers to the lat. of Paris and to a height of 60 m. above the sea's level, they become:

		Jolly	Regnault
Oxygen	.	1·429388	1·429802
Nitrogen	.	1·257873	1·256167

The *Bureau Internat. des Poids et Mesures* adopts for the weight of 1 litre of dry air under a normal barometric height of 1 mm. and at the normal temperature τ

$$P_{\tau i} = \frac{1·293052}{1 + 0·00367} + \frac{1}{760}$$

on the assumption that the air contains ·0004

parts of carbonic acid, and that ·00367 is the coefficient of expansion of air at constant pressure for a normal degree.

This expression is obviously only true for a particular ratio of oxygen and nitrogen. The composition of the air varies sufficiently to affect its value at different times (Ph. v. Jolly, *W.* 6, 520).

The pressure exerted by the atmosphere upon the earth's surface, at the sea's level or upon any substance at that level, may be expressed by saying that it is equivalent to a barometric column about 76 centimetres (29·92 inches) high. Now at ordinary temperatures 1 c.c. of mercury weighs 13·58 grams. If we suppose that the base of the mercurial column is 1 sq. centimetre it follows that the weight of the counterbalancing atmospheric column is $76 \times 13{\cdot}58 = 1032$ grams. This is equivalent to 14·73 lbs. upon a sq. inch. It can be readily calculated that the total weight of the atmosphere of this average pressure is about $11\frac{2}{3}$ trillions of pounds, or $5\frac{1}{4}$ trillion kilos. Allowing for the space occupied by the land above the sea's level, the mass of the atmosphere may be taken as $\frac{1}{1200000}$ part of that of the earth (Herschel).

The heights of the counterbalancing columns of air and mercury will of course be in the same ratio as the weights of equal volumes if it be assumed that the air is of uniform tension throughout. The height of this homogeneous atmosphere is between five and six miles: it was first calculated by Robert Boyle to disprove the conjectures of Kepler and others that the air could not extend beyond a couple of miles or so from the earth's surface.

As the air is an elastic fluid it follows from Boyle's law that its pressure must diminish as we ascend; hence the mercurial column stands lower on a mountain top than in the valley below. The fact that the barometric column is less on the top of an elevation than at the bottom was first noticed in 1643 by Claudio Bereguardi from observations on the tower of Pisa—that is, five years before Perrier made his famous experiments on the Puy-de-Dôme. The relation between the pressure and density of the air at different altitudes may be seen from the following table:—

Metres above sea level	Bulk of air	Density	Barometer mm.
0	1 cub. metre	1·	760
5,520	2 „	0·5	380
11,040	4 „	0·25	190
16,560	8 „	0·125	95
22,080	16 „	0·0625	47·5
27,600	32 „	0·0312	23·8

A pressure equivalent to the average pressure of the atmosphere at the level of the sea is frequently adopted by engineers and others as a *unit of pressure* and is styled *an atmosphere.* In this country an atmosphere is the pressure equal to 29·905 inches of mercury at 32° F. at London, and is about 14·73 lbs. on the sq. inch. In the metric system it is the pressure of 760 mm. (29·922 inches) of mercury at 0°C at Paris, and is equal to 1·033 kilos on a sq. centimetre. Hence the English 'atmosphere' is 0·99968 that of the metric system.

That the mercury in the Torricellian tube, or *barometer* as it was termed by Boyle, is constantly varying in height even at the same place, and that these variations are due to the fluctuating pressure of the atmosphere, appears to have been first clearly recognised by Descartes and by Boyle in 1658. It is, however, only within the last few years that we have acquired any very definite information respecting the distribution of the mass of the atmosphere over the earth. The pressure of the air at any given spot depends upon its relative position on the earth's surface: at this spot it varies also with the season of the year and the hour of the day. According to Buchan, whose isobaric charts are really the foundation of our exact knowledge of the subject, there are two broad belts of high pressure passing completely round the globe, one to the north and the other to the south of the equator. The southern belt of high pressure is nearly parallel to the equator; but the northern belt is more irregular in outline in consequence of the unequal distribution of land and water in the northern hemisphere. Between them is the low pressure of the tropical regions, through the centre of which is a narrow belt of still lower pressure towards which the north and south trades blow. A region of low pressure exists also round each pole; that round the north pole having two distinct centres, one in the north Atlantic, the other in the Pacific: at each of these the diminution of pressure is much below the average of the north polar depression. As regards the seasons, it is found that in January the highest pressures are over the continents of the northern hemisphere, and the lowest pressures are over the northern portions of the Atlantic and Pacific, S. America and S. Africa, and the Antarctic Ocean. The maximum mean pressure at this time is found in Central Asia where it is 30·4 inches, the minimum is in the N. Atlantic and round Iceland, where it is only 29·34 inches. The area of high pressure passes westwards through central and southern Europe, over the N. Atlantic between the parallels of 5° and 45°, across N. America (except to the North and North West), and over some portion of the Pacific. In July the mean pressure of Central Asia is only 29·468 inches or one inch less than in January. The lowest pressures of the western hemisphere are now to be found over the continents, whilst the highest are over the ocean between 50° N. lat. and 50° S. lat. Pressures are also higher at this time over S. Africa and Australia.

Speaking generally, atmospheric pressure is more regular throughout the year over the ocean than over the land. To the westward of each continent there is at all seasons an area of higher pressure over the ocean than over the land, in amount varying from 0·1 to 0·3 inch. These regions of high pressure extend over about 30° of longitude and attain their maxima during winter. The prevailing winds and the general circulation of the atmosphere are intimately associated with these areas of high and low pressure. Winds, in fact, are caused by the flowing away of air from regions of high pressure to those of low pressure, in accordance

with Buys-Ballot's law, which has been thus expressed by Buchan. 'The wind neither blows round the space of lowest pressure in circles returning on themselves, nor does it blow directly towards that space, but it takes a direction intermediate, approaching, however, more nearly to the direction and course of circular curves than of radii to a centre. More exactly the angle is not a right angle, but from 45° to 80°.'

The most important of the influences affecting atmospheric pressure during the months are temperature, and, as a secondary effect of temperature, humidity. By comparing the average pressure during the two months which exhibit the greatest divergence of temperature, viz. January and July, Buchan finds the following general result:—The January pressure exceeds that in July over the whole of Asia except in the north east, the highest pressures being near the middle of the continent; over Europe to the south and east of a line drawn from the north of Russia to the south of Norway, thence to the north coast of Germany, across France to Bordeaux, along the north of Spain, and passing out into the Atlantic at Corunna; over N. America except in the N. East and N. West. The July pressure exceeds that in January over the whole of the southern hemisphere, over the northern portion of the N. Atlantic, and over the northern part of the Pacific. The pressure which is thus removed from Asia, Europe, and America in the northern hemisphere in July is transferred partly to the southern hemisphere, and partly to the more northerly portions of the Atlantic and Pacific Oceans.[1]

At all places on the earth's surface where the alternation of day and night exists, the pressure of the atmosphere exhibits a remarkable diurnal variation. Generally speaking, the pressure is highest at about 9 A.M. and 9 P.M., and lowest at about 3 A.M. and 3 P.M., but the exact times vary somewhat with the locality and with the season of the year. The regularity of this variation within the tropics is so great that, as Humboldt remarked, the hour of the day may be approximately ascertained from the height of the mercurial column. This oscillation in atmospheric pressure is not confined to the sea's level: it takes place with equal regularity at heights of 13,000 feet. Within the tropics the oscillation amounts to about 2·2 mm., but as we approach the poles it decreases, until at 70° N. lat. it is only 0·3 mm. In our latitudes these horary variations are much less strongly marked than in the tropics, and are usually masked by climatic disturbances; but by comparing the results of a large number of observations, the fluctuation, which in these islands amounts to about 0·5 mm. on the mean of the year, can be clearly made out. In Paris eleven years' observation shows that the mean barometric oscillation amounts from 9 A.M. to 3 P.M. to 0·756 mm., and from 3 P.M. to 9 P.M. to 0·373 mm. The amount of the diurnal variation differs during the seasons of the year, being greater in summer than in winter. This peculiar phenomenon has given rise to much discussion, but as yet the cause cannot be said to be satisfactorily determined. Unlike the oceanic tide, it cannot be ascribed to the influence of the moon, since Bouvard has shown that the portion of the horary oscillation of the pressure of the atmosphere which depends on the attraction of the moon cannot raise the mercury in the barometer at Paris more than 0·018 mm., whilst the total variation deduced from the 11 years' observation amounts to 1·129 mm. The fact that the two maxima of pressure occur when the temperature is about equal to the daily mean, and the two minima when the temperature is at its highest and lowest, has led to the supposition that the fluctuations in pressure are connected with the daily march of temperature, and also with the humidity of the air. Dove, Sabine, and Hopkins have offered explanations based on such connections, but they are insufficient to account for the facts. Lamont and Brown have sought to refer the phenomenon to the magneto-electric influence of the sun, or in other words to connect it with the cause of the diurnal changes in terrestrial magnetism. There is every reason for supposing that the cause of the diurnal variation in atmospheric pressure is in some way dependent on, or originates with, the sun, but that its effects are greatly modified by a variety of local or accidental circumstances, as for example the prevailing winds, the amount of moisture in the air, and the relative distribution of land and water.

The atmosphere appears to receive its heat (1) from the direct rays of the sun, (2) by the reverberation of those rays from the surface of the earth, (3) by contact with the ground, and (4) through the influence of aqueous vapour.

Although the air is not absolutely diathermanous, the heat received by the air from the direct rays of the sun is the least important of the sources enumerated. We know very little at present as to whether the diathermancy of air varies with its density: that is, we have little evidence to determine whether the absorption of the sun's rays increases as they pass further into an atmosphere compressed by its own weight.

The greater portion of the heat which finds its way into the atmosphere is due to radiation from the earth's surface and to the air being in contact with the ground. The amount of heat thus sent into the air depends to a great extent on the nature of the soil which receives the solar radiations and on its capacity for retaining heat. Hence places in the same latitudes and not very far distant from each other, and in the same condition as regards protection, may have very different mean temperatures on account of the different capacities of various soils for absorbing and retaining heat.

Aqueous vapour is one of the most important agents in modifying the temperature of the atmosphere. A relatively large amount of heat is rendered latent in the process of evaporation from the surface of the earth, and becomes sensible on the condensation of the vapour in the upper regions of the air. Aqueous vapour also acts even when in the condition of a perfect gas

[1] For further details see Buchan, 'The mean pressure of the Atmosphere and the prevailing Winds over the Globe for the Months of the Year' (*T.E.* 25); also Julius Hann's *Erdkunde*; and R. H. Scott's *Elementary Meteorology*.

by retarding the transmission of the sun's rays through the air. As the quantity of aqueous vapour decreases as we ascend through the atmosphere, it follows that the amount of this absorption increases as the sun's rays penetrate further into the atmosphere.

The temperature of the atmosphere varies with a multitude of causes, such as the latitude, the season of the year, the hour of the day, the degree of humidity, &c. Among the causes which tend to raise the temperature of the air may be enumerated: the proximity of a western coast in the temperate zone; the divided configuration of a continent into peninsulas with deeply indented bays and inland seas; the aspect or position of a portion of the land with reference either to a sea of ice spreading far into the polar circle, or to a mass of continental land of considerable extent lying in the same meridian, either under the equator or at least within a portion of the tropical zone; the prevalence of southerly or westerly winds on the western shore of a continent in the temperate northern zone; chains of mountains acting as protecting walls against winds coming from colder regions; the infrequency of swamps which in the spring and beginning of summer long remain covered with ice; and the absence of woods in a dry sandy soil; finally the constant serenity of the sky in the summer months; and the vicinity of an oceanic current bringing water which is of a higher temperature than that of the surrounding sea.

On the other hand, the following causes lower the temperature of the air of a place: elevation above the level of the sea, when not forming part of an extended plain; the vicinity of an eastern coast in high and middle latitudes; the compact configuration of a continent having no littoral curvatures or bays; the extension of land towards the poles into the regions of perpetual ice without the intervention of a sea remaining open in the winter; a geographical position in which the equatorial and tropical regions are occupied by the sea, and consequently the absence under the same meridian of a continental tropical land having a strong capacity for the absorption and radiation of heat; mountain chains whose form and direction impede the access of warm winds; the vicinity of isolated peaks occasioning the descent of cold currents of air down their declivities; extensive woods which hinder the insolation of the soil by the vital activity of their foliage, which produces great evaporation owing to the large surface it exposes, and increase the surface that is cooled by radiation, acting consequently in a three-fold manner—by shade, evaporation, and radiation; the frequency of swamps or marshes which in the north form a kind of subterranean glacier in the plains lasting till the middle of summer; a cloudy summer sky which weakens the action of the solar rays; and finally a very clear winter sky favouring the radiation of heat (Humboldt: *Recherches sur les Causes des Inflexions des Lignes Isothermes*. See also Mohn's *Grundzüge der Meteorologie*).

The temperature of the air varies in different strata of the mass, decreasing generally after a certain elevation in proportion as the distance **from the earth's surface increases, but it is not possible to connect the diminution in temperature with the elevation in accordance with any definite law. It is usually assumed that the temperature falls about 1°C. for every 300 feet of perfectly dry air. As, however, the air invariably contains moisture, which is condensed by cooling and so produces heat, the decrement may be taken practically at about 1°C. for every 500 feet. This estimate can only be taken as an extremely rough approximation, for it is obvious that the rate of cooling must be affected by a great variety of causes.** Indeed the extensive series of aeronautical observations made at the instance of the British Association showed such great irregularities in the rate of diminution that Mr. Glaisher concluded that no law exists.

The atmosphere always contains free electricity, which is generally positive, that is, of an opposite kind to that of the earth. Atmospheric electricity increases rapidly after sunrise, and reaches its first maximum for the day at about 8 A.M. In general the variation in potential follows the diurnal range of atmospheric pressure. In summer the hours of maxima appear to be 8 A.M. and 10 P.M. and the minima 4 A.M. and 4 P.M. In winter the hours of maximum intensity are 9 A.M. and 10 P.M. and the minima 4 A.M. and 4 P.M. This diurnal variation seems to depend mainly on the degree of humidity of the air, the humid months manifesting the greatest potential. The potential seems to increase from July to January, and then to decrease. According to Everett, the maxima occur in February and October, and the minima in June and November.

In clear weather the air is usually positively electrified; it is only during rain, or more properly speaking when rain begins, that the electricity is negative. On the approach of a storm the air is almost invariably negatively electrified, even when the storm-clouds are at a considerable distance from the place of observation. When rain begins, the drops show negative electricity like the air. In light rain the potential is moderate, but heavy rain is almost invariably accompanied by a high potential. Dellmann's observations have shown, however, that the air may have a very high potential, extending over many days, without any other evidences of an approaching storm.

The sources from which the electricity of the atmosphere is derived are not clearly recognised. De la Rive attributed it mainly to chemical action at work on the earth; Pouillet to the evaporation of water; Volta and Saussure to the inequalities of atmospheric temperature. In all probability atmospheric electricity is not wholly due to any one of these causes: they may all be regarded as contributing to the amount.

The sun's light in its passage to the earth is partially absorbed and reflected by the atmosphere. Clausius has calculated that of the direct sunlight entering the atmosphere on a clear day 6·4 p.c. is absorbed, 18·6 is reflected and diffused, leaving therefore 75 p.c. to reach the earth. This light is, of course, refracted in its passage in amount depending upon the density of the air. Each ray entering the atmosphere otherwise than perpendicularly may be

supposed to describe a curve in coming to the earth, and as objects are seen in the tangent of the curve on entering the eye, all celestial bodies not in the zenith appear further removed from the horizon than they actually are.

The refractive power of dry air free from carbonic acid is the mean of the refractive powers of the oxygen and nitrogen under the pressure which each gas exerts in the mixture. This fact furnishes a proof of the physical nature of the atmosphere; since, as Dulong has shown, the refractive power of a compound gas is not equal to the refractive powers of its components, but is sometimes greater and sometimes less. Moist air is rather less refractive than dry air: precipitated vapour, as mist or fog, slightly increases the refractive power.

Although many of the more striking physical properties of the air were recognised even in the earliest ages, it is only within comparatively recent time that anything very definite has been known concerning its chemical nature.

It had long been observed that many metals on exposure to fire lost their peculiar lustre, and it was also known that by the prolonged action of heat they were ultimately converted into *calces* or earthy powders often possessing characteristic colours. The fact that the calx weighs more than the metal from which it was derived was known to Geber, and was well understood by the alchemists of the 16th century. Cardan (1506–1576) in noticing the increase of weight which accompanies the calcination of lead, says that it is due to a gas (*flatus*) which feeds flame and rekindles a body presenting an ignited point; and Cesalpinus in the *De Metallicis* (published at Nuremberg in 1602) also states that the 'crasse' which forms on the surface of lead exposed to heated air contains an aerial substance which increases the weight of the metal. Rey of Perigord seems to have first clearly recognised that the augmentation in weight was due to the action of the air. 'Je responds et soutiens glorieusement que ce surcroît de poids vient de l'air qui dans le vase a été épaissi.' Hooke in 1665 asserted that air contains a principle analogous to if not identical with that contained in nitre, and he seems to have believed that a certain portion only of the air is required to support combustion and respiration. The conception of the complex nature of the air was greatly strengthened by the observations of Mayow on respiration: his experiments are so precise and his facts so incontestable that, to quote Chevreul, one is surprised that the truth was not fully recognised until a century after his researches. Boyle also considerably extended our knowledge of the physical and chemical constitution of the air in the various treatises which he published between 1672 and 1692.

Two years after the sagacity of Rutherford had demonstrated the existence of nitrogen, Priestley obtained oxygen gas by heating the calx of mercury or red precipitate. The significance of this discovery in its relation to the constitution of the air and true nature of calcination was first clearly and irrefragably demonstrated by Lavoisier. By heating mercury in contact with a measured volume of air, he showed that about one-fifth of the volume of the air is absorbed by the metal with the formation of 'red precipitate,' from which the gas can be recovered by heating to a still higher temperature, and that the remaining four-fifths had all the properties of the 'mephitic air,' or nitrogen, of Rutherford. This experiment not only demonstrated the compound nature of the air and the character of its constituents, but it also showed approximately the relative quantities in which these constituents were present. It was of course quickly recognised that the active properties of air depended upon oxygen, and it was reasonable to assume that the relative amount of this gas determined the quality of air; hence arose the art of eudiometry. Priestley, who discovered nitric oxide in 1772, had observed that this gas became red in contact with the air and that the ruddy gas, unlike nitric oxide, was readily soluble in water. When it was subsequently ascertained that the formation of the soluble red gas was due to the action of oxygen on the nitric oxide, the idea of basing a eudiometric method upon this reaction was suggested by Priestley. Careful experimenters were, however, unable to distinguish air which was reputed to be unhealthy from that which experience had proved to be beneficial and salubrious. Thus, in Priestley's hands, air from the country seemed no better than that obtained from the worst-ventilated workshops of Birmingham. Cavendish, after a critical examination of the method, made numerous analyses of air. 'During the last half of the year 1781,' he says, 'I tried the air of near sixty different days in order to find whether it was sensibly more phlogisticated at one time than another, but found no difference that I could be sure of, though the wind and weather on these days were very various, some of them being very fine and clear, others very wet, and others very foggy . . . On the whole, there is great reason to think that the air was in reality not sensibly more dephlogisticated on any one of the sixty days on which I tried it than the rest.' Cavendish devised a scale of graduation applicable to all nitric oxide eudiometers, by means of which the late Dr. Wilson calculated that the mean of his results furnished the following numbers, expressing the centesimal composition of the air by volume:

Oxygen . . .	20·833
Nitrogen . .	79·167
	100·000

Cavendish concludes his account of these observations by pointing out the character of the information furnished by the eudiometer. Etymologically the name was without significance. 'In so far as the instrument takes cognisance of the impurity of the atmosphere, it betrays no difference between one specimen of air and another; so that, apparently, there are no degrees of goodness to be measured . . . . Thus it may be inferred that our sense of smelling can, in many cases, perceive infinitely smaller alterations in the purity of the air than can be perceived by the nitrous test' (Cavendish, 'Account of a New Eudiometer,' *T.* 1783).

These conclusions were confirmed by Humboldt and Gay-Lussac in their celebrated

memoir on the composition of the air, published in 1804. They employed the eudiometric method of Volta, *i.e.* explosion with hydrogen, and from an extensive series of analyses made on air collected in the most variable weather they concluded that 100 vols. of air contained 21 of oxygen and 79 of nitrogen.

The constant proportion of the two principal constituents of the atmosphere appeared now to be so well established that many chemists, after the recognition of the atomic theory, were inclined to think that air was a definite compound of oxygen and nitrogen. The two main constituents of the air are, however, not present in the simple ratio demanded by the law of Gay-Lussac. There is no evidence of chemical combination on mixing oxygen and nitrogen in the proportion in which these gases are present in air: the properties of the mixture are identical with those of air and are such as might be predicated to result from such a mixture. Moreover, oxygen and nitrogen can be isolated from air by mechanical means, or by taking advantage of the different intestinal movements of the gases. Graham separated the gases by atmolysis, and Bunsen demonstrated that the two gases were absorbed by solvents on which they exerted no chemical action in exact accordance with the law of partial pressures. Lastly the more accurate eudiometric processes of the last forty years have shown that the proportion of oxygen to nitrogen even in so-called normal air is not absolutely constant. This fact was first clearly demonstrated by Bunsen: in a series of analyses made during January and February 1846, he found that the percentage amount of oxygen varied from 20·97 to 20·84 by volume, *i.e.* a difference of 0·13 p.c., whereas the error of experiment never exceeded ·03 p.c. Even wider variations were found by Regnault in the course of a long series of analyses made on air collected in different parts of the world. In more than 100 analyses of air taken at various times of the year in and about Paris the lowest quantity of oxygen found was 20·913 and the highest 20·999; an extreme difference of 0·086; the experimental error being 0·02 p.c. Air collected from different parts of Europe, from valleys and from the tops of mountains and during different seasons of the year, showed variations in the amount of oxygen from 20·903 to 21·0 p.c.

Angus Smith found similar differences in London air in the course of numerous analyses made during 1869; the percentage amount of oxygen varied between 20·857 and 20·95. That these variations are due to local or accidental causes in the case of a town is established by the circumstance that the air in the streets is almost invariably poorer in oxygen than the air of the parks and open spaces. As types of normal air, Angus Smith found the following means of numerous analyses of air in Scotland (1863-5):

	Oxygen
Seashore and the heath	20·999
Tops of hills	20·98
Not mountainous	20·978
Forests	20·97

In marshy places the oxygen sank as low as 20·922.

In Glasgow, in a series of 30 analyses the oxygen varied from 20·889 in the closer parts to 20·929 in the more open places. A. R. Leeds found that the air of New York showed variations from 20·821 to 21·029 p.c.; and lastly Jolly found that air in Munich freed from carbonic acid and aqueous vapour varied in weight as much as 9 mgm. per litre, this variation depending upon the direction of the wind. By eudiometric measurement he obtained variations from 20·53 to 21·01 p.c. Southerly winds as a rule showed a relatively low percentage of oxygen. According to E. W. Morley these deficiencies in the relative amount of oxygen are to be attributed to the down-rush of air poorer in oxygen from the higher regions of the atmosphere. It was conjectured by Dalton and Babinet that air in the upper strata of the atmosphere contained relatively less oxygen than that immediately above the earth.

From Regnault's observations it would seem that sea-air contains slightly less oxygen than land air. The mean of 17 samples collected in the Arctic seas was 20·91, the extremes being 20·94 and 20·85. The mean of all the samples collected at sea was 20·84; in a series of twenty only five showed amounts of 20·96 and upwards. On the other hand, the observations of Lewy indicate that sea-air differs but little in composition from land-air, but that in the tropics it experiences close to the sea a diurnal variation in the amount of oxygen and carbonic acid, due to the action of the sun's heat in disengaging these gases from the water. Subsequent experiments on the composition of air over the sea have not confirmed these observations so far as the carbonic acid is concerned (*vide infra*).

We have comparatively little information in regard to the relative quantities of the constituents of the air at great heights. Such experimental evidence as exists seems to indicate that air contains relatively less oxygen in the higher strata than near the surface of the earth.

Very little is known respecting the proportion of *ozone* in the atmosphere, or of the circumstances which influence its production. The ozonometric methods hitherto devised are incapable of affording accurate quantitative estimations. Air over marshes or in places infested by malaria contains little or no ozone. No ozone can be detected in towns or in inhabited houses.

Houzeau (*A. Ch.* [4] 27, 5) determines the relative amount of ozone in the air by exposing strips of red-litmus paper dipped to half their length in a 1 p.c. solution of potassium iodide. The paper in contact with ozone acquires a blue colour from the action of the liberated potash upon the red litmus. The iodised litmus paper is preferable to iodised starch paper (Schönbein's test-paper) which exhibits a blue coloration with any reagent which liberates iodine, *e.g.* nitrous acid, chlorine, &c. From observations made with iodised litmus paper Houzeau concludes that ozone exists in the air normally, but the intensity with which it acts at any given point of the atmosphere is very variable. Country air contains at most $\frac{1}{450000}$ of its weight or $\frac{1}{700000}$ of its volume of ozone.

The frequency of the ozone manifestations varies with the seasons, being greatest in spring, strong in summer, weaker in autumn, and weakest in winter. The maximum of ozone is found in May and June, and the minimum in December and January. In general ozone is more frequently observed on rainy days than in fine weather. Strong atmospheric disturbances, as thunder storms, gales, and hurricanes, are frequently accompanied by great manifestations of ozone. According to Houzeau atmospheric electricity appears to be the most active cause of the formation of atmospheric ozone.

The existence of *hydrogen peroxide* in air was first established by Meissner in 1863, but we have no knowledge of the proportion in which it is present. All information as to its relative distribution is obtained from determinations of its amount in rain water and snow. The proportion seems to vary, like that of ozone, with the seasons of the year and with the temperature of the air. It is not improbable that the amount of hydrogen peroxide in air is greater than that of ozone, and it is possible that many so-called ozone manifestations are in reality due to peroxide of hydrogen (*v.* Houzeau, *C. R.* 76, 491; Schönbein, *J. pr.* 106, 270; Meissner, *J.* 68, 181; Schöne, *B.* 12, 346; 13, 1503).

The amount of *aqueous vapour* in the air is subject to great variations. It depends principally upon the temperature, on the distance from the equator, and on the level of the sea; on the form in which the aqueous vapour is precipitated; on the connexion between such precipitations and the change of temperature; and on the direction and succession of winds. The air is rarely saturated with aqueous vapour. In our moist climate saturation is sometimes very nearly attained, but in some parts of Central Asia, Russia, and Africa, extraordinary degrees of dryness have been noticed. In these islands the most humid month is January, and the dries is May.

The existence of *carbonic acid* in the atmosphere was first inferred by Dr. Macbride of Dublin, in 1764, from the observation that quicklime after exposure to the air effervesced on treatment with an acid. From the ease with which determinations of its amount may be effected our knowledge of the distribution of atmospheric carbonic acid and of the causes which affect its proportion is probably more precise than in the case of any other constituent of the air. In fresh country air the amount is remarkably constant, and may be stated as about ·034 p.c. In large towns and cities it is usually greater; thus Angus Smith, from numerous analyses made in London during November 1869, found as a mean ·044 p.c.: in upwards of 70 analyses the proportion fell below ·04 p.c. on only 5 occasions. In Glasgow, Smith found on an average ·05 p.c. The amount will of course be affected by any circumstances which interfere with the rapid diffusion of the carbonic acid produced by respiration and the combustion of fuel: hence during fogs the proportion is very greatly increased, an amount as high as 0·1 p.c. having been occasionally noticed. Smith gives the following summary of results obtained in Manchester (*Air and Rain*, p. 52).

	Per cent.
In Manchester streets in usual weather	·0403
During fogs	·0679
Where the fields begin	·0369

In country air the amount of carbonic acid is invariably greater at night than during the day. This remarkable diurnal variation was first pointed out by Saussure (*P.* 19, 391), and has been fully confirmed by subsequent observers. Thus, as the mean of numerous analyses made at Clermont-Ferrand, Truchot (*C. R.* 77, 675) obtained during the day ·0353, and during the night ·0403 (*v.* also G. F. Armstrong, *Pr.* 1880. 343; and Muntz a. Aubin, *C. R.* 92, 1299). These differences are mainly due to the exhalation of carbonic acid from plants at night. In the air of towns, and in the absence of vegetation, no such diurnal variations can be detected.

The amount of carbonic acid in the air is not sensibly altered by rain: this indeed would follow from the law of partial pressure. Over the sea the amount of carbonic acid is about ·03 p.c., and, contrary to the statement of Lewy, no diurnal variation in the amount can be perceived (Thorpe, *C. J.* [2] 5, 189). Schulze (*Landw. Versuchs.-St.* 14, 366) obtained similar results with sea air at Rostock: the mean of a large number of observations made from 1868 to 1871 was ·0292 p.c. No definite change in the amount was observed at different seasons of the year or at different times of the day. Fog and also a fall of snow were often associated with an increase of carbon dioxide (*v.* also Fittbogen a. Hasselbarth, *C. C.* 1874. 694).

Very little is known concerning the distribution of carbonic acid in the higher strata of the atmosphere. According to Saussure and Schlagentweit the amount of carbonic acid on the mountains is greater than on the plains: Truchot, however, found only ·0203 on the top of the Puy-de-Dôme (1446 m.), and ·0172 on the Peak of Sancy (1884 m.), as against ·0313 at Clermont-Ferrand. Additional observations are required.

The existence of *nitric acid* in the air was first inferred by Priestley. The amount, however is so small that it can only be detected in rain-water. Nitroxygen compounds are occasionally produced during thunder-storms, and it is said that the rain collected during a storm often contains notable quantities of nitrous and nitric acids. Boussingault found that a million parts of rain water contained 0·83 parts of nitric acid. Reichardt found in hailstones collected during a thunderstorm 0·526 parts per million.

According to Barral each hectare at Paris receives annually from the rain about 63·6 kilos of combined nitric acid. Bineau found that 1 litre of rain-water at Lyons contained in winter 0·3 mgm. nitric acid; in spring 1·0; in summer 2·0 mgm.; and in autumn 1·0 mgm. Bobierre found that a cubic metre of rain-water collected at Nantes in 1863 contained on an average 7·36 grams in the upper part, and 5·682 grams in the lower part, of the town (*C.R.* 1864, 755). Angus Smith (*Air and Rain*, p. 287) obtained the following results from a large number of observations on rain-water.

	Nitric acid (pts. per million)
Scotland: inland country places	0·305
Ireland—Valentia	0·370
England—sea coast country places	0·371
Scotland „ country places, west	0·372
„ „ „ east	0·476
„ „ „ average	0·424
Liverpool	0·582
England: inland country places	0·749
London: 1869	0·840
England: towns	0·863
Manchester: mean of 1869 and 1870	1·032
Scotland: towns (Glasgow excluded)	1·164
Glasgow	2·436

The amount of nitric acid in the rain-water of towns is uniformly greater than in rain-water collected in the country, from which we infer that much of the nitric acid in the air is due to the oxidation of ammonia derived from the decomposition of nitrogenous organic matter.

The *ammonia* in the air exists partly as carbonate, partly as nitrate and nitrite; ammonia itself being converted into nitrous and nitric acids and water by ozone. Scheele observed that a bottle containing hydrochloric acid became coated near the stopper with a film of sal ammoniac on exposure to the air. A piece of pipe-clay heated to redness and exposed to the air for a few days yields a perceptible amount of ammonia when reheated: this is not the case if the clay is kept in a stoppered bottle.

The quantity of ammonia contained in the air is extremely variable: the results on record differ from 135 to 0·1 of ammonia (calculated as carbonate) in 1,000,000 parts of air. Fresenius found that a million parts by weight of air contained during the day 0·098 parts of ammonia, and during the night 0·169 parts. According to H. T. Brown the amount ordinarily present is much larger than this: a million parts of country air at a height of 2 metres from the ground contained from 5·1 to 6·08 parts; the same amount of town air contained from 4·06 to 8·73 parts of ammonium carbonate (*Pr.* 18, 286). Direction of wind appears to have no influence on the amount. The quantity decreases after heavy rain but is restored to the normal amount (about 6 pts. in 1,000,000) in a few hours. Truchot (*C. R.* 77, 1159) found from 0·93 to 2·79 mgm. per cubic metre in the air of Auvergne, the highest results being obtained on misty days and the lowest on clear days. From observations made on the Puy-de-Dôme, Truchot concludes that the quantity increases with the elevation and is greater in cloudy than in clear air. On the other hand, Muntz and Aubin (*C. R.* 95, 788), from observations made on rain-water, find that the upper strata of the air contain much less ammonia than air near the surface of the earth. Nitric acid also was entirely absent from rain water collected at an elevation of 2877 m. Lewy (*C. R.* 91, 94) finds that the air in summer contains invariably larger quantities of ammonia (2·3 mgm. NH_3 in 1000 c.m.) than in winter (1·7 mgm. in 1000 c.m.).

The proportion of ammonia contained in rain water is as might be expected subject to equally wide variations. Lawes and Gilbert found that 1,000,000 pts. of rain-water collected in the country contained from 0·927 to 1·142 pts. of ammonia. Water collected in towns always contains much larger amounts than that collected in the country. Barral found that 1,000,000 parts of Paris rain-water contained 3·49 pts. of ammonia. Angus Smith obtained 1·07 pts. of ammonia in the rain-water of inland country places in England, whereas the water collected in the inland country places and more sparsely populated districts of Scotland contained only 0·53 pts. of ammonia per million. The rain water of London contained 3·45; that of Liverpool 5·38; that of Manchester 6·47; and that of Glasgow 9·10 parts per million. The larger proportion in the cities is due to the influence of animal life and to the constant presence of azotised organic matter in the air of thickly populated districts. Dews and fogs and snow always contain larger quantities of ammonia than rain-water. (For references, see Angus Smith, *Air and Rain.*)

In addition to these substances · oxygen, nitrogen, carbon dioxide, ozone, water-vapour, ammonia, and nitrous and nitric acids—which are the essential and necessary constituents of atmospheric air, it frequently contains a variety of accidental substances such as common salt, alkaline sulphates, and organic matter dead and living, derived from the proximity of the sea and of marshy districts, or to the influences of towns. Moscati nearly 80 years ago observed that the dew condensed on bottles filled with ice and suspended over the rice-fields of Tuscany, when collected quickly became putrescent and deposited flakes of a body containing nitrogen; and similar appearances were noticed by Rigaud de Lisle in 1812 in the dew collected in the marshes of Languedoc. The water deposited flakes of nitrogenised organic matter and gave with silver nitrate a precipitate which became immediately purple. (Compare A. H. Smee, *Pr.* 20, 442.) Vogel also observed that the moisture condensed on cold surfaces in inhabited rooms quickly became putrid owing to the presence of organic matter resembling albumin. Angus Smith found that the moisture condensed from breath after standing for some time formed a thick glutinous mass, which was seen under the microscope to be a closely-matted confervoid growth. Between the stalks of the confervæ a number of greenish globules were to be seen in a state of constant movement; also various species of volvox accompanied by monads many times smaller. As far back as 1722, Loewenhoeck (*Opera omnia*, vol. i. 1722) showed that rain-water, even when recently collected, contained infusoria derived apparently from the air. Similar observations were made by Ehrenberg and Gaultier de Claubry (*C. R.* 41, 645). The first attempt to throw light upon the question of the relative distribution of the organisms present in air was made by Pasteur, by subjecting certain putrescible solutions to the action of the air obtained from various localities.

Tyndall (*Les Microbes*, Paris, 1882) has shown that the micro-organisms contained in air are rapidly deposited in the absence of any strong aerial currents. Upon this fact Hesse (*Mittheilungen aus dem kaiserlichen Gesundheitsamte*: Berlin, 1884) has based a method for quantitatively estimating the relative pro-

portion of micro-organisms in air. The method consists in aspirating air through wide-mouthed glass tubes, coated internally with gelatine-peptone, prepared according to Koch's method, which is afterwards kept at a temperature of 20°-26° for a few days, when the organisms which have been arrested—consisting of the various monads, bacilli, and micrococci, capable of development and growth in the nutrient gelatine—are recognised by the colonies to which they give rise. By means of this method Dr. Percy F. Frankland has made a number of estimations of the micro-organisms contained in the air of towns, and in the country, and in inhabited buildings. By simultaneously exposing small circular glass dishes partially filled with the nutrient gelatine to the action of the air, a rough estimate was obtained not only of the number of micro-organisms in a given volume of the air, but also of the number which fell during a given time on a definite horizontal area. As the mean of a series of observations made on the roof of the South Kensington Museum between Jan. and June 1886, it was found that there were 35 organisms in ·10 litres of air, whilst 279 was the average number which fell in 1 sq. ft. in 1 minute. Similar experiments made near Reigate and in the vicinity of Norwich showed an average of 14 organisms in 10 litres of air, whilst 79 fell per sq. ft. per minute. Experiments made in Kensington Gardens, Hyde Park, and on Primrose Hill, gave an average of 24 organisms in 10 litres, and a deposition of 85 per sq. ft. per minute. At St. Paul's Cathedral, 56 organisms were found at the base, 29 in the Stone Gallery, and 11 in the Golden Gallery, in 10 litres of air. At Norwich Cathedral 18 at the base, 9 at a height of 180 ft., and 7 at 300 ft. In inhabited buildings great variations were observed; as a rule the number of micro-organisms was less than that found in the open air when the air of the room was undisturbed, but rose rapidly when the air was set in motion by draughts or by the presence of many people (P. F. Frankland, *Pr.* 40, 509).

Angus Smith has sought to base a system of chemical climatology on the examination of rain-water collected under different conditions and at various places. Rain falling through the air over the sea always contains common salt and sulphates, the latter in larger proportion to the chlorides than is found in sea-water. The sulphates increase inland: they seem to be a measure of the products of decomposition, the sulphuretted hydrogen which is evolved in the putrefaction of certain organic compounds being oxidised in the atmosphere. In large towns, the amount of the sulphates is greatly increased owing to the combustion of coal containing iron-pyrites. Indeed the rain water of large towns is frequently acid from the presence of free sulphuric acid. When rain contains 40 parts per million of free acid, vegetation is rapidly affected. The following analyses by Angus Smith will serve to show the general character of the rain-water (and therefore of the impurity of the atmosphere) in various parts of Great Britain. The results, which are the mean of many experiments, are expressed in parts per million of rain-water.

	I.	II.	III.	IV.	V.	VI.	VII.
Sea Air:							
Scotland	12·28	3·61	0	0·74	0·105	·424	·018
England	not det.	5·88	0	1·90	not det.	·371	not det.
Inland cntry. air:							
Scotland	3·37	2·06	0	0·53	·04	·305	·264
England	3·99	5·22	0	1·07	·109	·749	·466
Towns:			0				
London	1·25	20·49	3·87	3·45	·205	·840	not det.
Liverpl.	10·16	39·59	11·56	5·38	·159	·582	3·896
Mnchstr.	5·83	44·82	10·17	6·47	·251	1·032	·4401
Glasgow	8·97	70·19	15·13	9·10	·300	2·436	10·040

I. Amount of hydrochloric acid (chlorides).
II. " sulphuric acid (sulphates).
III. " acidity (free sulphuric acid).
IV. " ammonia.
V. " albuminoid ammonia; decomposition of organic matter.
VI. " nitric acid.
VII. " weight of oxygen required to oxidise organic matter (measure of organic matter and nitrites).

Although the atmosphere is subject to continual change from a multitude of causes, such as the respiration of animals and plants, the combustion of organic matter, various processes in the arts &c., still from its immense mass and uninterrupted motion such changes have only the very slightest effect on its composition. Let us very briefly consider the chief circumstances which tend to influence the proportion of its components.

Nitrogen is undoubtedly a primitive substance: no other body occurs in such large quantities as an element. This gas is probably the source of all nitrogenous bodies, in the formation of which it is continually abstracted from the air. A portion only of the nitrogen so abstracted finds its way back to the air as such: the most considerable compensating influence known to us is the nitrogen evolved by volcanoes.

By the respiration of animals and the oxidation of the spent portions of their tissue, by the respiration of plants at night-time, and by the combustion of fuel, large quantities of carbonic acid are being continually added to the atmosphere. Enormous quantities also are evolved from volcanoes and other subterranean sources. Poggendorff has indeed calculated that the amount so added is at least ten times as much as is derived from all other sources put together. Taking the weight of carbonic acid in the air as ·06 per cent., it can be calculated from the area of the terrestrial oblate spheroid that the weight of the carbonic acid in the atmosphere is about 3,225,000 × 10 kilos (Le Conte, *P.M.* [5] 15, 46; *v.* also E. H. Cook, *P. M.* [5] 14, 387). At least 50,000 million kilos of carbonic acid are daily added to the air. The main compensating influence is of course the action of growing plants in sunshine; carbon dioxide is also removed directly and indirectly by zoophytes and by certain chemical actions such as the conversion of felspar into kaolin, &c. Sterry Hunt ('Chemical and Geological Relations of the Atmosphere,' *Am. S.* 1880) has calculated that a weight of carbonic acid equal to more than twenty-one times that of our present atmosphere would be absorbed in the production from orthoclase of a layer of kaolin extending over the earth's surface with a thickness of 500 metres, an amount representing

but a small proportion of the results of felspathic decay in the sedimentary strata of the globe.

Dumas and Boussingault, in their well-known memoir on the *Composition of the Air* (*A. Ch.* [3] 3) made some interesting calculations on the duration of the supply of atmospheric oxygen. They found that, taking all the known sources of diminution, and assuming that the oxygen disengaged by plants compensates only for the causes of diminution at present unknown, then even in this exaggerated case three times the amount of oxygen thus abstracted would only amount in 100 years to about $\frac{1}{8000}$ of the total quantity, an amount barely appreciable by our most exact eudiometric methods.—T. E. T.

ATOMIC AND MOLECULAR WEIGHTS.— Two theories regarding the ultimate constitution of matter have opposed each other from the beginnings of philosophy; one asserts that any mass of apparently homogeneous matter is really homogeneous; the other affirms that every portion of matter of sensible size is built up of a vast number of small particles which are not themselves capable of further sub-division. The earliest exponent of the second theory of whom we possess any definite record was the Greek philosopher Democritus, who flourished about 450 B.C. The doctrines of Democritus were developed by Epicurus, and the teachings of the Epicurean philosophy are preserved in the Latin poem of Lucretius (B.C. 99-55). These early atomists tried to assign to the atoms, of which they said matter is composed, only such properties as should suffice for their presentation in time and space. They taught that nothing exists save atoms and empty space; that the atoms or 'first-beginnings,' are of many different forms, and different weights, and the number of atoms of each form is infinite; that all change is only combination or separation of atoms; and that the atoms are in constant motion. To meet the objection that if a mass of matter is at rest the parts of it cannot be in motion, Lucretius uses the illustration of a flock of grazing sheep with skipping lambs; to one looking from a distance the flock appears as a white motionless patch on the green hillside, but a closer view shows that the parts of the flock are continually changing their positions. Every atom, Lucretius asserts, is indestructible, and its motion is indestructible likewise; if this were not so how could we account for the preservation of fixed types in nature? Roses always bear roses, and each animal reproduces its like, because the 'first beginnings' (or atoms) of which each is composed are the same and are never destroyed or worn out. 'First-beginnings are of solid singleness, and in no other way can they have been preserved through ages during infinite time past in order to reproduce things.' [1] Here we see how clearly the early atomists recognised that every event in nature occurs in accordance with strict laws. Nothing happens by chance, was a fundamental doctrine of these philosophers. 'I . . . teach . . . by what law all things are made, what necessity there is then for them to continue in that law, and how impotent they are to annul the binding statutes of time.' [1] The way to gain a knowledge of the laws of nature, Lucretius teaches, is to examine natural events. (See for instance the analysis of the effects of the thunderbolt in Book vi. 323-398.) The differences between a hard body such as iron, and a soft body such as air, depend, according to Lucretius, on the motions of the atoms of the two bodies; in the hard body the atoms move to and fro within very small distances, in the soft body they move freely and rebound from each other only at comparatively long intervals. 'Bodies are partly first-beginnings of things, partly those which are formed by a union of first beginnings.' [2] The latter are produced by the atoms grouping themselves *in concilio*; this term seems to mean something very like our expression *in combination*. The properties of the body formed by the grouping together of atoms need not resemble the properties of the atoms themselves (see, for instance, Book I. 915-920). Not only must the atoms enter into *concilium* with each other in order that any kind of matter may be produced, but the properties of the matter thus formed depend on the mutual relations of the atoms; 'it matters much with what others and in what positions the same first-beginnings of things are held in union, and what motions they do mutually impart and receive.' [3]

Although this theory was so nearly complete, yet, as taught by Lucretius, it had few of what we now regard as the essential features of a good scientific theory; it was not stated in terms which permitted of numerical applications to actual phenomena. Few or no exact applications of the theory could be made to natural phenomena. It was scarcely able to predict events in nature except in a wide and loose way. It savoured too much of a dogma. It was rather a speculation as to what might be the cause of natural occurrences, than an attempt to determine what these causes really were.

The teachings of the Epicurean philosophers were opposed by those of the school of Aristotle. The Aristotelians magnified the names of things and made them as real or even more real than the things themselves; they identified 'modes of predication with modes of existence' (Lange). Matter occupied a foremost position in the Epicurean scheme of the universe, but by the followers of Aristotle it was regarded only as the 'potentiality of becoming anything or everything.' Aristotelianism prevailed in the middle ages and atomism fell more and more into disrepute.

But in 1592, Gassendi, Canon and Provost at Digne in Provence, revived the atomic theory of the Greek philosophers, and attempted to found on it an interpretation of natural events. The influence of Gassendi was continued through Newton and Boyle; the former of whom, as we know, demonstrated that not only do masses of matter attract each other, but that every particle of each mass attracts every particle of the other mass with a force varying directly as the masses of the particles and inversely as the square of the distance between the particles. As Newton accepted the atomic conception of the structure of matter, his demonstration of the action of the force of gravitation gave a new

[1] Lucretius, *De Rerum Natura*, I. 548-550 (Munro's translation).

[1] Id. V. 55-58. [2] Id. I. 483-4. [3] Id. II. 1007-9.

point of departure for the theory of atoms. From this time a science of atomic physics became possible. But the difficulty was, and still is, to form a clear mental picture of the mechanism of the action of the force of gravitation in terms of the atomic conception of matter. Newton gave the mathematical construction, and clearly separated this from the physical explanation which belonged to the region of conjecture.

Not much was done, after Newton, to advance the application of the atomic theory until the early years of the present century, when Dalton made a serious attempt to determine the conditions under which the atoms of elementary bodies unite to form the atoms of compound bodies.

The great advance made by Dalton consisted in his asserting the possibility of finding the relative weights of the atoms of all kinds of matter, and in his demonstration of the method whereby these relative weights could be determined.

Many analyses of chemical compounds had been made before the time of Dalton; the results were usually stated in percentages, and they seemed to have but few mutual relations. Richter (1791–1802) had shown that a definite mass of each acid combines with a specified mass of a given base; he had arranged several acids and bases in order of neutralisation. Fischer, in 1803, published a table of chemical equivalents which expressed the quantities of bases which were of equal value as regarded power of neutralising a constant quantity of a specified acid. Lavoisier, Cavendish, and others, had to some extent grasped the conception of the elements combining in definite proportions. They had never doubted that every chemical substance was of definite composition, and that it would be possible by careful analyses of many compounds to find the laws of elementary combinations. Proust had analysed several pairs of oxides of the same metal; from some of his numbers the law of combining weights might have been deduced, had he stated his results so as to show the quantities of oxygen in combination with a fixed quantity of metal.

Dalton analysed two compounds of carbon and hydrogen, and found that in one there was twice as much hydrogen as in the other, combined with the same quantity of carbon. He found similar regularities in the quantities of oxygen which combined with a specified quantity of carbon, in the quantities of oxygen which combined with a specified quantity of nitrogen, &c. Meanwhile he had been thinking much regarding the ultimate particles of bodies; he had pictured to himself a quantity of gaseous matter as resembling a heap of small shot, as built up of little definite parts or atoms. He saw how the facts of chemical combination he had been studying would help him to find the relative weights of these small particles. Dalton's genius recognised the unity which bound together so many diverse physical and chemical facts. He at once stated clearly the quantitative laws of chemical combination and referred these laws to one underlying conception, the conception namely of the atom. 'In all chemical investigations it has justly been considered an important object to ascertain the relative *weights* of the simples which constitute a compound. But unfortunately the inquiry has terminated here; whereas from the relative weights in the mass, the relative weights of the ultimate particles or atoms of the bodies might have been inferred, from which their number and weights in various other compounds would appear, in order to assist and to guide future investigation, and to correct their results. Now it is one great object of this work to show the importance and advantage of ascertaining the relative weights of the ultimate particles both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle.'[1]

That he might determine the relative weight of the 'ultimate particle' of an element it was necessary for Dalton to have some means of fixing the number of particles of that element in one 'ultimate particle' of several of its compounds. Thus, masses of hydrogen and oxygen combine in the ratio of 1 to 8; now, if we assume that the ultimate particle, or atom, of water is 9 times heavier than the atom of hydrogen, the most probable conclusion is that one atom of water is formed by the union of one atom of hydrogen, the mass of which is taken as unity, with one atom of oxygen, the mass of which is 8 times that of the hydrogen atom; but if we choose to assume that the atom of water is 16 times heavier than that of hydrogen, then the experimental results—1 of hydrogen combines with 8 of oxygen, by weight—are most readily interpreted by saying that one atom of water is formed by the union of 2 atoms of hydrogen, weighing 2, with one atom of oxygen, weighing 16. We cannot then determine how many times the atom of oxygen is heavier than that of hydrogen unless we have previously determined how many times the atom of the compound formed by the union of hydrogen and oxygen, that is the atom of water, is heavier than the atom of hydrogen.

Dalton framed certain empirical rules regarding the composition of the atoms of compounds formed by the union of two elements. His principal rules were these: 'If there are two bodies, A and B, which are disposed to combine, the following is the order in which combination may take place, beginning with the most simple, namely:

1 atom of A + 1 atom of B = 1	atom of	C,	binary;
1 atom of A + 2 atoms of B = 1	„	D,	ternary;
2 atoms of A + 1 atom of B = 1	„	E,	ternary;
1 atom of A + 3 atoms of B = 1	„	F,	quaternary;
3 atoms of A + 1 atom of B = 1	„	G,	quaternary.'
&c. &c.			

'1st. When only one combination of two bodies [elements] can be obtained, it must be presumed to be a *binary* one, unless some cause appears to the contrary.

'2nd. When two combinations are observed they must be presumed to be a *binary* and a *ternary*.

'3rd. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*.

'4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, &c. &c.'

'From the application of these rules to the

[1] Dalton, *A New System of Chemical Philosophy* (1808).

chemical facts already well ascertained, we deduce the following conclusions: 1st. That water is a binary compound of hydrogen and oxygen, and the relative weights of the two elementary atoms are as 1:7 nearly [more correctly 1:8]. 2nd. That ammonia is a binary compound of hydrogen and azote, and that the relative weights of the two atoms are as 1:5 nearly [more correctly 1:4·66]. . . . In all these cases the weights are expressed in atoms of hydrogen, each of which is denoted by unity."[1] But even if these rules were admitted, it was not always possible to fix the relative weight of an elementary atom; thus, two compounds of carbon and oxygen were known to Dalton, containing, according to his analyses, 2·7 parts by weight of carbon combined with (i) 7 and (ii) 3·5 parts by weight of oxygen; hence, by rule 2, the first of these is a compound of one atom carbon with one atom oxygen, and hence the atomic weight of carbon is 2·7, and the second is a compound of 2 atoms carbon ($=5·4$) with 1 atom oxygen ($=3·5\times 2$). But the results of analyses might also be stated thus: (i) 5·4 carbon + 14 oxygen, (ii) 5·4 carbon + 7 oxygen; and the conclusion might be drawn that the first is a compound of 1 atom carbon (5·4) with 2 atoms oxygen (7×2), and the second is a compound of 1 atom carbon (5·4) with one atom oxygen (7). Both ways of stating the results of experiments would be in keeping with Dalton's rules, but the first would lead to the number 2·7, and the second to the number 5·4, as representing the relative weight of the atom of carbon. Another objection to the Daltonian rules of atomic syntheses was that, although to-day we may know of but one compound of two specified elements, to-morrow we may know of several compounds of these elements.

Berzelius continued the work which Dalton had begun; his aim was to discover the laws of atomic combinations. Why does a specified element by combining with oxygen produce only two or perhaps three different oxides? Why do not the elementary atoms combine in a great many different ratios? What are the limiting forms of the compound atoms produced by the union of any specified elementary atoms? Berzelius busied himself with such questions as these. And that he might find some solutions to such questions, Berzelius was obliged to frame empirical rules, as Dalton had done before him.

The following may be taken as an example of the Berzelian rules. If an element forms two oxides with twice as much oxygen by weight in one as in the other, relatively to a fixed mass of the element, the atom of that compound which contains the smaller mass of oxygen is to be regarded as composed of one atom of oxygen and one atom of the specified element, and the atom of the other compound is to be regarded as composed of two atoms of oxygen and one atom of the specified element; but if the masses of oxygen in the two oxides are in the ratio 2:3 relatively to a specified mass of the other element, then the atom of the compound with less oxygen is to be regarded, as before, as composed of one atom of oxygen and one atom of the specified element, but the atom of the compound with more oxygen is to be regarded as composed of three atoms of oxygen and two atoms of the other element.

But such rules were only empirical, and, however satisfactory might be the particular results obtained by their application, it was impossible to rest contented until some general principle had been attained which should admit of universal application. In the course of his inquiries regarding the syntheses of atoms, Berzelius performed a vast number of very careful analyses, the results of which firmly established the quantitative laws of chemical combination. These laws (*v.* COMBINATION, CHEMICAL, LAWS OF) assert:—(1) that the masses of the constituents of every homogeneous kind of matter stand in an unalterable proportion to one another, and also to the mass of the compound they produce—the mass of the compound being always equal to the sum of the masses of the constituents; (2) that when two elements combine to form more than one compound, the masses of one of the elements which combine with a constant mass of the other element bear a simple relation to each other; and (3) that the masses of different elements which combine with one and the same mass of another element are also the masses of these different elements which combine with each other, or they stand in a simple relation to those masses. These laws may all be expressed in the statement that the elements combine only in the ratios of their combining weights, or, in simple multiples of these ratios. By the combining weight of an element is here meant the smallest mass of that element which is found to combine with one part by weight of hydrogen or with 8 parts by weight of oxygen.

As Berzelius was pursuing his investigations into the gravimetric composition of compounds, Gay-Lussac was making experiments on the volumetric composition of gaseous compounds. In 1809 this naturalist was able to prove (1) that the volumes of the gaseous elements which combine to form a gaseous compound stand in an unalterable proportion to each other; (2) that when two gaseous elements combine to form more than one gaseous compound, the volumes of one of the elements which combine with a constant volume of the other element bear a simple relation to each other; and (3) that the volumes of different gaseous elements which combine with one and the same volume of another gaseous element are also the volumes of these different elements which combine with each other, or they stand in a simple relation to those volumes. These laws may all be expressed by saying that the gaseous elements combine only in the ratios of their combining volumes, or in simple multiples of these ratios. By the combining volume of a gaseous element is here meant the smallest volume of that element which is found to combine with one unit volume of hydrogen, and a unit volume of hydrogen is defined to be the volume, at normal temperature and pressure, occupied by one unit mass of this element.

Gay-Lussac argued that the ratios of the masses of the combining volumes of gaseous elements are also the ratios of the masses of the atoms of these elements; and the conclusion

[1] Dalton, *l.c.*

was drawn that equal volumes of gaseous bodies, measured at the same temperature and pressure, contain equal numbers of atoms. This conclusion, if admitted, seems to put into our hands a means for finding the relative masses of the atoms of many compounds and hence of many elements. But the application leads to unlooked-for results. Consider the case of hydrogen and oxygen: experiment shows that two volumes of hydrogen—weighing two—combine with one volume of oxygen—weighing 16—and produce two volumes of water-gas—weighing 18; hence, if equal volumes of gases contain equal numbers of atoms, two atoms of hydrogen—weighing two—combine with one atom of oxygen—weighing 16—and the product is two atoms of water-gas—each weighing 9. But each of these atoms of water-gas contains atoms of hydrogen and oxygen; now, the atom of oxygen has been shown to weigh 16 times as much as the atom of hydrogen; hence the atom of water-gas contains half an atom of oxygen. Again, consider the case of hydrogen and chlorine: experiment shows that one volume of hydrogen—weighing one—combines with one volume of chlorine—weighing 35·5—and that the product is two volumes of hydrochloric acid weighing 36·5; hence, if equal volumes of gases contain equal numbers of atoms, one atom of hydrogen has combined with one atom of chlorine to produce two atoms of hydrochloric acid. But as each atom of hydrochloric acid is composed of both hydrogen and chlorine, it follows that each atom of hydrochloric acid is formed by the union of half an atom of hydrogen and half an atom of chlorine. But these conclusions are at variance with the fundamental definition of the atom, which states that the atom is the smallest mass of a body that can exhibit the properties of that body.

The discovery that gaseous elements combine in fixed quantities by volume had done something to advance the study of atomic synthesis, but it had not removed the fundamental difficulty, the difficulty, namely, of finding some generally applicable principle by means of which the relative weights of the ultimate particles, or atoms, of compounds might be determined. This difficulty was overcome by Avogadro. In 1811 this Italian naturalist introduced into chemistry the conception of two orders of small particles—the *molecule*, and the *atom*. The molecule of an element or a compound, said Avogadro, is the smallest mass of it which exhibits the properties of that element or compound; the molecule of an element or a compound is formed by the union of smaller particles of matter which we shall call atoms; in the case of the molecule of an element the atoms are all of one kind, in the case of the molecule of a compound the atoms are of two, or more than two, different kinds. As the properties of the molecule of a compound are very different from the properties of the atoms which compose it, so it is probable that the properties of the molecule of an element are different from the properties of the atoms by the union of which the molecule is produced. A chemical action between two gases was conceived by Avogadro as being separable, in thought if not in actuality, into two stages; in the first stage the molecules of the reacting gases are shattered, and in the second stage the parts of these molecules, that is the atoms, are rearranged to form the molecules of the new bodies.

Avogadro modified the generalisation made by Gay-Lussac, and re-stated it thus:—'*Equal volumes of gases, temperature and pressure being the same, contain equal numbers of molecules.*' The reactions between hydrogen and oxygen, and hydrogen and chlorine, which could not be explained by the generalisation of Gay-Lussac, are perfectly consistent with the generalisation of Avogadro. Two volumes of hydrogen combine with one volume of oxygen, and the product is two volumes of water-gas; that is, in terms of Avogadro's statement, $2p$ molecules of hydrogen, each composed of x atoms, combine with p molecules of oxygen, each composed of x' atoms (x may or may not equal x'), and the product is $2p$ molecules of water-gas. One volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid; that is, in terms of Avogadro's statement, p molecules of hydrogen, containing x atoms, combine with p molecules of chlorine, containing x' atoms (x may or may not equal x'), to form $2p$ molecules of hydrochloric acid.

Not only are these, and other, reactions, between gases explicable in terms of the generalisation of the Italian naturalist, but this statement gives us a means of determining the relative masses of the molecules of all gaseous bodies, and also of determining the minimum number of atoms in each of these molecules. That is to say, the generalisation of Avogadro gives us what we could not obtain from the rules of Dalton or Berzelius, or from the generalisation of Gay-Lussac. For it is evident that, if the number of molecules in equal volumes of two gases is the same, the masses of the two kinds of molecules must be in the same ratio as the densities of the two gases; and hence, if the density of one of the gases be taken as unity, the density of the other, in terms of this one, expresses the relative mass of a molecule of this other gas. Let the two gases be hydrogen and oxygen; experiment shows that a given volume of oxygen is sixteen times heavier than the same volume of hydrogen; hence, if equal volumes contain equal numbers of molecules, a molecule of oxygen is sixteen times heavier than a molecule of hydrogen. Let us call the mass of a molecule of hydrogen one, then, in order to find how many times greater than the mass of this molecule is the mass of the molecule of any gas, we have only to determine the density of the specified gas in terms of hydrogen as unity; the number expressing the density of the gas expresses also the relative mass of the molecule of the gas. But, further, the generalisation of Avogadro puts into our hands a means whereby the minimum number of atoms in a gaseous molecule may be determined, and hence a means whereby the maximum relative values to be assigned to the masses of atoms may be determined. Consider the mutual action of hydrogen and chlorine, hydrogen and bromine, nitrogen and hydrogen, and oxygen and hydrogen. Having regard only to the volumes of the reacting gaseous elements and the volumes of the

gaseous compounds produced, the actions in question may be stated thus:—

(i.) One volume of hydrogen combines with one volume of chlorine to produce two volumes of hydrochloric acid; (ii.) One volume of hydrogen combines with one volume of bromine-gas to produce two volumes of hydrobromic acid; (iii.) one volume of nitrogen combines with three volumes of hydrogen to produce two volumes of ammonia; (iv.) one volume of oxygen combines with two volumes of hydrogen to produce two volumes of water-gas.

Now, as equal volumes contain equal numbers of molecules, these statements may be put as follows:—

(i.) p molecules of hydrogen combine with p molecules of chlorine, and the product is $2p$ molecules of hydrochloric acid; (ii.) p molecules of hydrogen combine with p molecules of bromine gas, and the product is $2p$ molecules of hydrobromic acid; (iii.) p molecules of nitrogen combine with $3p$ molecules of hydrogen, and the product is $2p$ molecules of ammonia; (iv.) p molecules of oxygen combine with $2p$ molecules of hydrogen, and the product is $2p$ molecules of water-gas.

Therefore in (i.) one molecule of hydrogen has produced, by union with chlorine, two molecules of hydrochloric acid, both of which are composed of hydrogen and chlorine; in (ii.) one molecule of hydrogen has produced, by union with bromine, two molecules of hydrobromic acid, both of which are composed of hydrogen and bromine; in (iii.) one molecule of nitrogen has produced, by union with hydrogen, two molecules of ammonia, both of which are composed of nitrogen and hydrogen; and in (iv.) one molecule of oxygen has produced, by union with hydrogen, two molecules of water-gas, both of which are composed of oxygen and hydrogen. In other words, in reactions (i.) and (ii.) every molecule of hydrogen has separated into at least two parts; in reaction (iii.) every molecule of nitrogen has separated into at least two parts; and in reaction (iv.) every molecule of oxygen has separated into at least two parts.

These parts of molecules are called atoms.

If we assume the truth of Avogadro's generalisation, then the foregoing reactions are most simply interpreted by saying that the molecules of hydrogen, nitrogen, and oxygen, are each built up or composed of two atoms. As hydrogen is the standard element to which the atomic and molecular weights of all other bodies are referred, we say that the *atomic weight of hydrogen is one*, and, because of such reactions as those just stated, that the *molecular weight of hydrogen is two*. But if the molecular weight of hydrogen is two, the molecular weight of oxygen must be 32, the molecular weight of nitrogen must be 28, the molecular weight of hydrochloric acid must be 36·5, the molecular weight of hydrobromic acid must be 81, the molecular weight of ammonia must be 34, and the molecular weight of water-gas must be 18; because oxygen is 16 times heavier than an equal volume of hydrogen, nitrogen is 14 times, hydrochloric acid is 18·25 times, hydrobromic acid is 40·5 times, ammonia is 17 times, and water-gas is 9 times, heavier than an equal volume of hydrogen.

By such reactions and such modes of reasoning as these, we arrive at the following practical definition of the molecular weight of a gaseous element or compound:—*The molecular weight of a gaseous element or compound is a number which expresses how many times greater than two unit masses of hydrogen is the mass of the specified element or compound which occupies (under the same conditions of temperature and pressure) the same volume as is occupied by these two unit masses of hydrogen.*

Determinations of the sp. gravs. of gases are subject to several sources of error. But the values to be assigned to the combining weights of the elements, that is, the masses of the elements which combine with one part by weight of hydrogen or 8 parts by weight of oxygen, can be determined with great accuracy. Now, it is evident that the molecular weight of an element must be equal to the combining weight of this element or to a simple multiple of this number, and that the molecular weight of a compound must be equal to the sum, or to a multiple of the sum, of the combining weights of its constituent elements; hence the data which are required for an *accurate* determination of the molecular weight of an element are (i.) an exact determination of the combining weight of the element, and (ii.) a measurement of the relative density of the element in the state of gas; similarly the data which are required for an *accurate* determination of the molecular weight of a compound are (i.) exact determinations of the combining weights of the constituent elements, and (ii.) a measurement of the relative density of the compound in the state of gas. Thus, 35·37 parts by weight of chlorine combine with 1 part by weight of hydrogen, therefore the molecular weight of chlorine is $n35{\cdot}37$; but a given volume of chlorine is 35·5 times heavier than an equal volume of hydrogen, therefore the molecular weight of chlorine is approximately $35{\cdot}5 \times 2 = 71$; now, $2 \times 35{\cdot}37 = 70{\cdot}74$; hence the molecular weight of gaseous chlorine is 70·74. Again, phosphorus hydride is composed of masses of phosphorus and hydrogen united in the ratio 10·32 to 1, therefore the molecular weight of this compound is $n11{\cdot}32$; but this compound in the state of gas is 17 times heavier than hydrogen, therefore its molecular weight is approximately equal to $17 \times 2 = 34$; now, $3 \times 11{\cdot}32 = 33{\cdot}96$; hence the molecular weight of gaseous phosphorus hydride is 33·96.

Having thus arrived, by the help of Avogadro's generalisation, at a definition of molecular weight, and having determined that the molecules of hydrogen, nitrogen, and oxygen, and of some other elements, are very probably composed each of two parts or atoms, we proceed to find an exact meaning for the term atom. If the atom is assumed to be the ultimate portion of any homogeneous kind of matter of which cognisance is to be taken in chemistry, then it is evident that a molecule of a compound gas, formed by the union of (say) three elements, A, B, and C, must be formed by the union of at least one atom of the element A, one atom of the element B, and one atom of the element C. In general terms, no molecule of a compound gas can be formed by the combination of less than a single atom of each of the elements by the union of which the compound in question is

produced. This is equivalent to saying, the atom of an element is the smallest mass of that element which combines with other atoms to produce a molecule.

We cannot as yet determine the absolute mass of the atom of any element, but we have agreed to call the mass of an atom of hydrogen unity, and to represent the masses of the atoms of other elements in terms of the atom of hydrogen; hence we arrive at the practical definition of the maximum atomic weight of an element as follows:—

The maximum atomic weight of an element is a number which expresses how many times greater is the smallest mass of that element which combines with other elements to form a compound gaseous molecule, than the smallest mass of hydrogen which combines with other elements to produce a compound gaseous molecule, such smallest mass of hydrogen being taken as unity.

The term, and the conception underlying the term, molecule, are applied to compounds and elements alike; the term, and the conception underlying the term, atom, are applied in strictness to elements only.

The foregoing definitions of atomic weight and molecular weight are practical, because they indicate the nature of the data which must be obtained before the atomic or molecular weight of a gaseous body can be found. Suppose it is required to find the molecular weight of oxygen; the mass of this element which combines with unit mass of hydrogen must be accurately measured; and the relative density of oxygen gas must be determined, the standard of reference being hydrogen taken as twice unity. Now, the relative densities of gases are determined by experiments in terms of air taken as unity; but a specified volume of air is 14·435 times heavier than the same volume of hydrogen at the same temperature and pressure; therefore the relative density of any gas referred to air as unity multiplied by 14·435 × 2 (= 28·87) gives the relative density of that gas referred to hydrogen as twice unity, that is, gives (approximately) the molecular weight of the gas. Let it now be required to determine the atomic weight of oxygen; the definition of atomic weight tells that the molecular weights of several gaseous compounds containing oxygen must be determined, that these compounds must be analysed and the results in each case stated in parts by weight of each element per molecule of the compound, and that the smallest mass of oxygen thus found in any molecule is to be taken as the atomic weight of oxygen. Here are some of the data which have been thus accumulated:—

Data for determining the atomic weight of Oxygen.

Gaseous compound	Sp. Gr. air=1	Sp. Gr. × 28·87; *i.e.* approximate molecular weight	Molecular weight	Analysis, stated in parts by wt. per molecule
Carbon dioxide	1·53	44·2	43·89	31·92 oxygen + 11·97 carbon
Sulphur dioxide	2·25	64·9	63·90	31·92 „ + 31·98 sulphur
Sulphur trioxide	2·9	83·7	79·86	47·88 „ + 31·98 „

Were these the only known gaseous compounds containing oxygen we should conclude that the atomic weight of oxygen is 31·92, that of hydrogen being unity. But the following numbers show that this conclusion is incorrect:—

Data for determining the atomic weight of Oxygen.

Gaseous compound	Sp. Gr. air=1	Sp. Gr. × 28·87; *i.e.* approximate molecular weight	Molecular weight	Analysis, stated in parts by wt. per molecule
Carbon monoxide	·97	27·97	28·93	15·96 oxygen + 11·97 carbon
Water	·63	18·2	17·96	15·96 „ + 2 hydrogen
Nitric oxide	1·04	30·0	29·97	15·96 „ + 14·01 nitrogen

These numbers show that at least three compounds exist the gaseous molecule of each of which contains 15·96 parts by weight of oxygen; hence, as no molecule is known containing less than this mass of oxygen, 15·96 is taken as the atomic weight of oxygen. Before, then, the atomic weight of an element can be determined with a fair degree of probability a number of gaseous compounds of the element must be analysed; if only a few gaseous compounds of a specified element are known it is probable that the value deduced, from analyses of these compounds, for the atomic weight of the element, is too large; it certainly cannot be too small. Thus, let us consider the data for finding the atomic weight of aluminium:—

Data for determining the atomic weight of Aluminium.

Gaseous compound	Sp. Gr. air=1	Sp. Gr. × 28·87; *i.e.* approximate molecular weight	Molecular weight	Analysis, stated in parts by wt. per molecule
Aluminium chloride	9·35	270·0	266·26	54·04 aluminium + 212·22 chlorine
„ bromide	18·6	537·5	532·54	54·04 „ + 478·5 bromine
„ iodide	27·0	780·0	813·22	54·04 „ + 759·18 iodine

*Specific Heats of the Solid Elements.**

Element	Spec. heat	Temp.	Atomic weight	Sp. ht. × at. wt.	Observer
Lithium	·941		7·01	6·6	Rg.
[1] Beryllium	·62	450° to 500°	9·1	5·6	He.
[2] Boron	?·5	about 1000°	10·9	5·5	Wb.
[3] Carbon	·463	980°	11·97	5·5	Wb.
Sodium	·293	−34° to +7°	23	6·7	Rg.
Magnesium	·245		24	5·9	Kp.
„	·25		„	6·0	Rg.
Aluminium	·202		27·02	5·5	Kp.
„	·214		„	5·8	Rg.
„	·225		„	6·1	Mt.
[4] Silicon	·203	232°	28	5·7	Wb.
Phosphorus *cryst.*	·174	−78° to +10°	30·96	5·4	Rg.
„ „	·189		„	5·9	Rg.
„ „	·202		„	6·2	Kp.
„ *red*	·170		„	5·3	Rg.
Sulphur	·188		31·98	6·0	D.P.
„ *rhombic*	·163		„	5·2	Kp.
„ „	·171		„	5·5	Bn.
„ „	·178		„	5·7	Rg.
[5] Potassium	·166	−78° to +10°	39·04	6·5	Rg.
Calcium	·170		39·9	6·8	Bn.
Titanium	·1485	0° to 300°	48	7·1	N.P.
[6] Chromium	·10		52·4	5·2	Kp.
[7] Manganese	·122		55	6·7	Rg.
Iron	·112		55·9	6·3	Kp.
„	·114		„	6·4	Rg.
„	·110		„	6·1	D.P.
Nickel	·108		58·6	6·3	Rg.
Cobalt	·107		59	6·3	Rg.
Copper	·093		63·4	6·0	Kp.
„	·095		„	6·1	Rg.
„	·095		„	6·1	D.P.
Zinc	·0932		64·9	6·1	Kp.
„	·0935		„	6·1	Bn.
„	·0955		„	6·2	Rg.
„	·093		„	6·0	D.P.
[8] Gallium	·079	12° to 23°	69	5·4	Bt.
Germanium	·077	0° to 200°	72·3	5·64	N.P.
Arsenic *amorphous*	·076‡		74·9	5·7	B.W.
crystalline	·083‡		„	6·2	B.W.
„	·0814		74·9	6·1	Rg.
„	·0822		„	6·2	N.
[9] Selenion *amorphous*	·0746	−27° to +8°	78·8	5·9	Rg.
crystalline	·0745	−18° to +7°	„	5·9	Rg.
„	·0762		„	6·0	Rg.
„	·0861		„	6·8	N.

Element	Spec. heat	Temp.	Atomic weight	Sp. ht. × at. wt.	Observer
Selenion *crystalline*	·084‡		78·8	6·7	B.W.
Bromine *solid*	·0843	−78° to −20°	79·75	6·7	Rg.
[10] Zirconium	·0666		90·0	6·0	M.D.
[11] Molybdenum	·0722		95·8	6·9	Rg.
Rhodium	·058		104	6·0	Rg.
Ruthenium	·0611		104·5	6·4	Bn.
Palladium	·0593		106·2	6·3	Rg.
Silver	·056		107·66	6·0	Kp.
„	·0559		„	6·0	Bn.
„	·057		„	6·1	Rg.
Cadmium	·0542		112	6·0	Kp.
„	·0548		„	6·1	Bn.
„	·0567		„	6·3	Rg.
Indium	·057		113·4	6·5	Bn.
Tin	·0548		117·8	6·5	Kp.
„	·0559		„	6·6	Bn.
„	·0562		„	6·6	Rg.
„	·0514		„	6·0	D.P.
Antimony	·0523		120·0	6·2	Kp.
„	·0495		„	5·9	Bn.
„	·0508		„	6·0	Rg.
„	·0507		„	6·0	D.P.
Tellurium	·0475		125	5·94	Kp.
„	·0474		„	5·94	Rg.
Iodine	·0541		126·53	6·8	Rg.
Lanthanum	·0449		138·5	6·2	Hd.
Cerium	·0448		141	6·3	Hd.
Didymium	·0456		144	6·5	Hd.
Tungsten	·0334		183·6	6·0	Rg.
Osmium	·0311		193	6·0	Rg.
Iridium	·0326		194	6·2	Rg.
Platinum	·0325		195	6·4	Kp.
„	·0324		„	6·3	Rg.
„	·0314		„	6·3	D.P.
[12] Gold	·0324		197	6·4	Rg.
[13] Mercury *solid*	·0319	−78° to −40°	199·8	6·4	Rg.
[14] Thallium	·0335		203·6	6·8	Rg.
Lead	·0307		206·4	6·3	Rg.
„	·0315		„	6·5	Kp.
„	·0314		„	6·5	Rg.
Bismuth	·0305		208	6·5	Kp.
„	·0308		„	6·3	Rg.
Thorium	·0276		232·4	6·4	Nn.
Uranium	·028		240	6·6	Zn.

* When no temp. is given the determinations were made somewhere between 0° and 100°, the numbers in these cases may be regarded as approximately representing the mean specific heats for the temperature-interval 40°-60°.

[1] The number for beryllium is that calculated by Humpidge from a series of determinations, at temperatures varying from 100° to 450°, made with a specimen of beryllium containing 99·2 per cent. of the metal. See further, p. 343.

[2] [3] [4] Spec. heats of boron, carbon, and silicon are discussed on p. 343–4.

[5] The higher temperature (+10°) is not given in Regnault's paper, but judging from the context it appears to be approximately correct.

[6] This number for chromium is probably too low; see Kopp, *A. Suppl.* 3, 77 (note).

[7] The specimen of manganese employed contained a little silicon.

[8] Spec. heat of molten gallium between 109° and 119° = ·0802 (Berthelot; *Bl.* [2] 31, 229).

[9] Spec. heat of amorphous selenion determined at high temperatures is abnormal, because of the large quantity of heat absorbed before fusion.

[10] Spec. heat of zirconium calculated by Mixter and Dana from determinations made with a sample containing known quantities of aluminium.

[11] The specimen of molybdenum employed contained carbon.

[12] Spec. heat of gold is nearly constant from 0° to 600°: at 900° Sp. ht. = ·0345, and at 1000° = ·0352 (Violle, *C. R.* 89, 702).

[13] Spec. heat of liquid mercury at 55° = 0·033 (Regnault).

[14] The specimen of thallium employed contained a little oxide.

The numbers marked with ‡ are probably too large. See Weber's papers referred to below.

The names of the various observers are abbreviated in the table:—

Rg.	stands for	Regnault.—His papers on spec. heat are to be found in	*A. Ch.* [2] 73, 5; [3] 1, 129; 9, 332; 26, 261; 38, 129; 46, 257; 63, 5; 67, 427.
Kp.	„	Kopp „ „	*A.* 126, 362; and do. *Suppl.* 3, 1 and 289.
N.	„	Neumann „ „	*P.* 126, 123.
Bn.	„	Bunsen „ „	*P.* 141, 1.
Wb.	„	Weber „ „	*P.* 154, 367 (translation in *P. M.* [4] 49, [161 and 276]).
D.P.	„	Dulong and Petit „ „	*A. Ch.* 10, 395.
Bt.	„	Berthelot „ „	*C. R.* 86, 786.
Hd.	„	Hillebrand „ „	*P.* 163, 71 (translation in *P. M.* [5] 3, 109).
B.W.	„	Bettendorf and Wüllner „ „	*P.* 133, 293.
M.D.	„	Mixter and Dana „ „	*A.* 169, 388.
Nn.	„	Nilson „ „	*B.* 15, 2619.
N.P.	„	Nilson and Pettersson „ „	*Z. P. C.* 1, 27.
Mt.	„	Mallet „ „	*C. N.* 46, 178.
Zn.	„	Zimmermann „ „	*B.* 15, 849.
He.	„	Humpidge „ „	*Pr.* 39, 1.

As no other gaseous compounds of aluminium, except these three, have been prepared in a state of purity and analysed, we conclude that the atomic weight of this metal is not greater than 54·04; but as only three gaseous compounds of aluminium are known, it is not unlikely that the true value to be assigned to the atomic weight of this element is $\frac{54\cdot04}{2}$ or $\frac{54\cdot04}{3}$ or $\frac{54\cdot04}{4}$, &c. The greater the number of compounds of a given element which have been gasified and analysed, the greater is the probability that the value thence obtained for the atomic weight of the element represents the true value of this constant.

Avogadro's generalisation—equal volumes of gases contain equal number of molecules—places in the hands of chemists an instrument whereby they may determine the relative weights of the molecules of all gaseous or gasifiable compounds and elements, and the maximum values to be assigned to the atomic weights of all elements which form gaseous or gasifiable compounds. But at present the densities of only 14 elements have been determined in the gaseous state, and gaseous compounds of only 42 different elements have been prepared and analysed. Hence the application of the method introduced by Avogadro is limited. There are two other methods of general applicability for determining the values to be assigned to the atomic weights of elements; let us consider these methods briefly.

In 1819 a paper was published by two French naturalists, Dulong and Petit, on the specific heats of 13 solid elements, viz., copper, gold, iron, lead, nickel, platinum, sulphur, tin, zinc, bismuth, cobalt, silver, and tellurium (*A. Ch.* 10, 395).

The products obtained by multiplying the generally accepted atomic weights of the nine elements from copper to zinc in this list by the specific heats of these elements, and sub-multiples of the generally accepted atomic weights of the remaining four elements by the specific heats of these elements, had all nearly the same value. Generalising from these results, Dulong and Petit concluded that 'the atoms of all the simple bodies have exactly the same capacity for heat.' This generalisation has, on the whole, been borne out by subsequent research.

The table on p. 342 contains most of the well-established data regarding the specific heats of solid elements in so far as direct determinations are concerned.

The values to be assigned to the specific heats of beryllium, boron, carbon, and silicon, have been the subject of many experiments and of much discussion: Nilson and Pettersson (*B.* 13, 1451; *v.* also *C. N.* 42, 297) made a series of determinations with a specimen of metallic beryllium containing about 5 per. cent. of beryllium and iron oxides. The following were the most important results:—

Specific Heat of Beryllium (Nilson & Pettersson).

Temp. interval	Spec. ht.	Spec. ht. × 9·1	Spec. ht. × 13·65
0°– 46	·3973	3·6	5·4
0 –100	·4246	3·86	5·8
0 –214	·475	4·26	6·4
0 –300	·5055	4·6	6·9

Nilson and Pettersson concluded from these numbers that the atomic weight of beryllium is 13·65; but L. Meyer (*B.* 13, 1780) showed that the true values for the spec. heat of this metal at various temperatures, as calculated from the data summarised in the preceding table, are as follows:—

Specific Heat of Beryllium (Meyer).

Temp.	Spec. ht.	Increase in spec. ht. for 1°	Sp. ht. × 9·1	Sp. ht. × 13·65
20·2°	·3973		3·62	5·43
		·00101		
73·2	·4481		4·08	6·12
		·00085		
157	·5193		4·73	7·10
		·00063		
256·8	·5819		5·29	8·94

These numbers show that the specific heat of beryllium increases as temperature increases, but that the rate of this increase is considerably less for the interval 157° to 256° than for that of 20° to 157°. Humpidge (*Pr.* 39, 1), working with a specimen of beryllium prepared with great care and containing 99·2 per cent. of the metal and ·7 per cent. of beryllium oxide, obtained the following results:—

Specific Heat of Beryllium (Humpidge).

Temp.	Spec. heat	Spec. ht. × 9·1
100°	·4702	4·28
200	·5420	4·93
400	·6172	5·61
500	·6206	5·65

The value approximates to a constant between 450° and 500°. There can now be little doubt that the specific heat of beryllium is considerably larger at high than at low temperatures, that this value is nearly constant at about 500° and upwards, and that at these temperatures beryllium is not an exception to the law of Dulong and Petit. (For more details *v.* BERYLLIUM.)

Very varying values had been obtained for the specific heats of the three elements, boron, carbon, and silicon, before the researches of Weber. The following table summarises the chief results:—

Specific Heats of Boron, Carbon, and Silicon (Weber's numbers not included).

(Temp. about 35°–55°)

	Spec. heat.		Sp. ht. × at. wt.	Observer.	Date.
BORON					
amorphous	·254		2·8	Kp.	1864
crystalline	·230		2·6	do.	do.
"	·252		2·8	M.D.	1873
"	·257		2·8	Rg.	1869
graphitic	·235		2·6	do.	do.
CARBON					
diamond	·143		1·7	B. W.	1868
"	·147		1·8	Rg.	1841
"	·366	Temp. 20°–1000°	4·4	Dewar	
graphite	·174		2·1	Kp.	1864
"	·188		2·3	B. W.	1868
"	·198		2·4	Rg.	1866
gas-carbon	·165		2·0	Kp.	1864
"	·186		2·2	B. W.	1868
"	·197		2·4	Rg.	1841
"	·32	Temp. 20°–1000°	3·8	Dewar	
SILICON					
fused	·138		3·9	Kp.	1864
"	·166		4·6	Rg.	1861
crystalline	·165		4·6	Kp.	1864
"	·171		4·8	M. D.	1873
"	·173		4·8	Rg.	1861

Weber, about 1872, made a careful series of determinations of the specific heats of these three elements (*P. M.* [4] 49, 161 and 276); his

more important results are presented in the following table:—

Specific Heats of Boron, Carbon, and Silicon (Weber).

	Temp.	Spec. heat.	Sp. ht. × at. wt.
Boron *crystalline*[1]	−40°	·1915	2·11
" "	+77°	·2737	3·01
" "	177°	·3378	3·72
" "	233°	·3663	4·03
Carbon *diamond*	−50°	·0635	0·76
" "	+10°	·1128	1·35
" "	85°	·1765	2·12
" "	250°	·3026	3·63
" "	606°	·4408	5·29
" "	985°	·4589	5·51
" *graphite*	−50°	·1138	1·37
" "	+10°	·1604	1·93
" "	61°	·1990	2·39
" "	201°	·2966	3·56
" "	250°	·325	3·88
" "	641°	·4454	5·35
" "	978°	·467	5·50
Porous wood carbon	0°–23°	·1653	1·95
" "	0°–99°	·1935	2·07
" "	0°–223°	·2385	2·84
Silicon *crystallised*	−40°	·136	3·81
" "	+57°	·1833	5·13
" "	128°	·196	5·50
" "	184°	·2011	5·63
" "	232°	·2029	5·68

These numbers show that the specific heats of boron, carbon, and silicon increase as temperature increases, but that, in each case, the value of this increase for a given temperature-interval is considerably less at high than at low temperatures. The observed variation in the rate of increase of the specific heat of crystallised boron[1] is nearly identical with the observed variation in the rate of increase of the specific heat of crystallised carbon for equal intervals of temperature up to 230-250°; if it is assumed that this identity remains at higher temperatures, then the specific heat of crystallised boron[1] may be calculated, from the observations made with crystallised carbon, at temperatures up to about 1000°. The value thus calculated for the specific heat of boron at 1000° is ·50. The specific heat of crystalline silicon attains an almost constant value at about 230°. (For more details *v.* Boron, Carbon, Silicon.)

Looking at the determinations of the specific heats of solid elements as a whole, it appears clear that the specific heat of any element varies with the temperature, and that the relation between the variation of specific heat and that of temperature differs for each element; and, moreover, that the value of the specific heat of an element depends to some extent on the physical condition of the element. But there seems certainly to be an interval of temperature for which the specific heat of an element attains a constant, or nearly constant, value; this temperature-interval varies for each element, especially for the non-metallic elements with small atomic weights; for many elements it may be approximately taken as 0° to 100°(C.). **For this interval of temperature only can any element be said to obey the law of Dulong and Petit.**

[1] There is, however, considerable doubt whether the material used by Weber was pure boron.

This law may now be stated in a practical form thus:—*The atomic heat, i.e. the product of specific heat, at the temperature-interval for which sp. ht. is nearly constant, into atomic weight, of all solid elements is nearly a constant, the mean value of which is* 6·4. If this is granted it follows that the atomic weight of any solid element is approximately equal to the quotient $\frac{6 \cdot 4}{\text{spec. heat}}$; provided that the specific heat of the element has been determined for a considerable range of temperature, and, if the specific heat has been found to vary considerably with variations of temperature, that the determinations have been continued until a constant, or a nearly constant, value has been obtained.

Attempts have been made to determine the specific heats of several elements by an indirect method. The method is based on the generalisation, $\frac{A.C}{n}$ = a constant (about 6·4); where A = the formula-weight of a solid compound, C = the specific heat of the compound, and n = the number of elementary atoms in the formula of the compound. This generalisation has been stated in various forms; the earliest appears to be that given by F. Neumann, in 1831: 'The amounts of chemically similar compounds expressed by their formulæ possess equal specific heats' (*P.* 23, 1). The statement is sometimes put thus: 'the molecular heat of a solid compound is equal to the sum of the atomic heats of its constituent elements;' by 'molecular heat' is here meant the product of the specific heat of the compound into the mass expressed by its formula. The form given above, $\frac{A.C}{n}$ = a constant, is the outcome of investigations made principally by Garnier (*C. R.* 35, 278; 37, 130), and Cannizzaro (*Bl.* 1863. 171).

As an example of the application of this generalisation, to find a value for the specific heat of an element in the solid form, let us take Kopp's calculation of the specific heat of solid chlorine (*A. Suppl.* 3, 321). The data are these:—molecular heats (as defined) of metallic haloid salts: RCl = 12·8, RBr = 13·9, RI = 13·4; RCl_2 = 18·5, RI_2 = 19·4. In each case R represents one atom of a metal the atomic heat of which is 6·4. The atomic heat of solid bromine = atomic heat of solid iodine = 6·6 (approximately). Now, as the metallic chlorides, bromides, and iodides, examined are chemically similar, and as the 'molecular heats' of the similar salts are nearly the same, Kopp has concluded that the atomic heat of solid chlorine is approximately equal to 6·4. This conclusion is in keeping with the observed values; thus: RCl (12·8) − R(6·4) = 6·4; RCl_2(18·5) − R(6·4) = 12·1, and $\frac{12 \cdot 1}{2}$ = 6·05. Further data are presented by the following 'molecular heats': $KClO_3$ = 24·8, $KAsO_3$ = 25·3. The argument here is, that as these values are nearly the same, and as the difference in composition between the two compounds is represented by the exchange of Cl for As, it follows that the atomic heat of solid chlorine is approximately

equal to that of arsenic; but the atomic heat of arsenic, as determined by direct experiment, is 6·1, hence the atomic heat of solid chlorine is approximately equal to 6·1.

This indirect method often leads, as might be expected, to several values for the specific (or atomic) heat of an element. Thus, from determinations of the 'molecular heats' of various oxides and other salts containing metals the atomic heat of each of which has been directly determined to be approximately 6·4, the following values for the atomic heat of solid oxygen are arrived at:

From	RO	4·6
,,	RO_2	3·7
,,	R_2O_3	4·8
,,	$KAsO_3$	4·2
,,	$KClO_4$	3·5 (assuming at. ht. of Cl = 6)
,,	$KMnO_4$	3·8

The mean of these values is 4·1.

The indirect method of finding the atomic heat of an element is undoubtedly useful, but no great stress can be laid on conclusions arrived at by this method only. It is certain that an erroneous conclusion regarding the value of the atomic weight of an element may be deduced from measurement of the specific heats of solid compounds of that element. For example, Donath determined the specific heat of uranoso-uranic oxide to be ·0798 (*B.* 12, 742); assuming the specific heat of solid oxygen to be 0·25 $\left(=\frac{4·1}{16}\right)$, the specific heat of uranium was calculated to be ·0497; now $·0497 \times 120 = 5·96$, therefore, as analyses of compounds had proved that the atomic weight of uranium is $n120$, it was concluded by Donath that the atomic weight of uranium is 120. But pure metallic uranium was prepared shortly afterwards, and the specific heat of this metal was directly determined to be ·028; now $·028 \times 120 = 3·3$, but $·028 \times 240 = 6·6$; hence the atomic weight of uranium is much more probably 240 than 120. The larger value (240) has been confirmed by the preparation and analyses of two gaseous compounds of uranium (*v.* regarding this subject, Kopp, *B.* 19, 813).

The following statements fairly summarise the results of the determinations of the atomic heats of the elements:

I. *Solid elements, 45 in number, the specific heats of which have been directly determined, and the atomic heats of which are all approximately equal to* 6·4: Li, Na, Mg, Al, P, S, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Zr, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, La, Ce, Di, W, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, U...(Cr).

II. *Solid elements, 6 in number, the specific heats of which have been directly determined, and vary considerably with temperature, and the atomic heats of which appear to be approximately equal to* 5·5: Ga (? inaccurately determined), Be, B, C, Si, Ge.

III. *Solid elements, 5 in number, the specific heats of which have been indirectly determined and the atomic heats of which are probably approximately equal to* 6·4: V, Rb, Sr, Cs, Ba.

IV. *Gaseous elements*; *specific heats in solid form very doubtful, and apparently variable*: H, (F), N, O, Cl.

It has been already shown that the application of Avogadro's law enables a maximum value to be found for the atomic weight of any element which forms one or more compounds gasifiable without decomposition. The maximum value thus found for the atomic weight of aluminium was 54·04; but as this value was based on analyses of only three gaseous compounds, it was asserted that the true value was possibly one-half or one-third, &c. of this number. Now, the specific heat of aluminium has been determined to be ·22; hence, assuming the law of Dulong and Petit, the atomic weight of aluminium must be approximately equal to 30 $(30 \times ·22 = 6·6)$; therefore the value $\frac{54·04}{2} = 27·01$ is assigned to the atomic weight of this metal. The maximum values assigned to the atomic weights of iron (111·8), copper (126·8), and gallium (138), by the application of Avogadro's law have, in each case, been halved when determinations have been made of the specific heats of these metals.

Various observations on the connexions between the chemical composition and the crystalline form of solid compounds had been made previous to the year 1819, in which year the 'law of isomorphism' was propounded by E. Mitscherlich; this law was subsequently modified and extended, and in 1821 Mitscherlich stated it as follows: 'Equal numbers of atoms similarly combined exhibit the same crystalline form; identity of crystalline form is independent of the chemical nature of the atoms, and is conditioned only by the number and configuration of the atoms.' Further research has shown that Mitscherlich's statement was too absolute. On the one hand, many solid compounds are known, the atomic compositions of which are very similar, and which, nevertheless, crystallise not only in different forms, but in different systems, thus:

$PbCrO_4$ is monoclinic, but $PbMoO_4$ is quadratic; AgCl and AgBr are regular, but AgI is hexagonal; KNO_3 is rhombic, but $CsNO_3$ and $RbNO_3$ are hexagonal.

On the other hand, many solid compounds crystallise in identical or very similar forms, and nevertheless exhibit unlike atomic compositions; thus the crystalline form of the following salts is the same: $K_2TiF_6H_2O$, $CuTiF_64H_2O$, $K_2NbOF_5H_2O$, $CuNbOF_54H_2O$, $K_2WO_2F_4H_2O$, $CuWO_2F_44H_2O$. Many ammonium salts crystallise in the same forms as the corresponding salts of potassium, but the number of atoms in one formula-weight of these salts is different. It is indeed somewhat difficult to give an exact meaning to the expression 'isomorphous crystals;' by this phrase some naturalists mean crystals any one of which is capable of growing in unmodified form when immersed in a solution of any other (Kopp, *B.* 12, 900 *et seq.*); others include crystals belonging to the same system but exhibiting very small differences in the measurements of their angles, *e.g.* the rhombohedral carbonates of magnesium, calcium, iron, zinc, and manganese; others even include crystals which very closely resemble each other but yet belong to different systems. The fact that the same compound may crystallise in two, or even three, distinct forms, further complicates the connexion between isomorphism and

chemical composition; thus, arsenious oxide, As_4O_6, and antimonious oxide, Sb_4O_6, both crystallise in regular octahedra and also in rhombic forms; titanium dioxide, TiO_2, crystallises in two forms belonging to the quadratic system, but exhibiting very different relations of crystalline axes, and also in a third form, viz. rhombic prisms.

The constituents of isomorphous compounds are sometimes themselves isomorphous; *e.g.* the double compounds $3Ag_2S.Sb_2S_3$ and $3Ag_2S.As_2S_3$ crystallise in identical forms, and the sulphides Sb_2S_3 and As_2S_3 also crystallise in identical forms. On the other hand, the constituents of isomorphous compounds are sometimes not isomorphous; *e.g.* the sulphates of magnesium, nickel, and zinc, crystallise in rhombic forms, but the oxides of magnesium and nickel crystallise in regular, and oxide of zinc, in hexagonal, forms. Isomorphism is sometimes not shown in comparatively simple analogous compounds of two elements, while the more complicated analogous compounds of the same elements crystallise in identical or very similar forms; *e.g.* many of the simpler compounds of cadmium are not isomorphous with the analogous compounds of the magnesian metals (Mg, Ca, Mn, Fe, Co, Ni, Zn, Cu), but the comparatively complex salts of cadmium, such as $CdSO_4.K_2SO_4.6H_2O$, are usually isomorphous with the analogous salts of the metals named. Hence it is necessary to distinguish strict isomorphism as applied to bodies which exhibit the same or nearly the same crystalline form, from the isomorphism of bodies which, although themselves crystallising in different forms, nevertheless combine with one and the same third body to produce compounds into which they enter as corresponding elements or groups, and which crystallise in the same forms (*v.* Kopp, *Lehrbuch der Physikal. Chemie*, 2, 141). The crystalline forms of several elements have been determined, but the statement that such or such elements form an isomorphous group usually means only that analogous compounds of these elements are for the most part isomorphous (*v.* ISOMORPHISM).

Notwithstanding the many qualifying clauses with which any general statement of the connexion between crystalline form and chemical composition must, at present, be guarded, it has frequently been found possible to use the knowledge we have of the connexion in question as a guide in researches concerning the atomic weights of elements. In these cases it is assumed that, as a general rule, those masses of two bodies which can mutually replace each other in compounds without change of the crystalline form of the compounds, or in other words those masses which are crystallographically equivalent, have similar atomic compositions. By compounds of similar atomic composition is here meant compounds which are very analogous in their chemical relations, and the formulæ of which contain equal numbers of atoms, or groups of atoms which react through series of changes as if each were a single atom.

Now, if the atomic weight of a specified element is known, and if experiment shows that the mass of this element expressed by its atomic weight is crystallographically equivalent to x unit masses of another element, it follows that the value of x is very probably the value of the atomic weight of the second element. Thus, the facts that gallium sulphate formed a double compound with ammonium sulphate, and that this double sulphate was isomorphous with the alums, indicated that the double sulphate in question was a true alum; hence the general formula which expresses the composition of alums expresses the composition of the double sulphate of gallium and ammonium. The formula in question is $X_23SO_4.M_2SO_4.24H_2O$, where M = an alkali metal or thallium; but in common alum $X_2 = Al_2 = 2 \times 27{\cdot}02$ parts by weight of aluminium; and in gallium alum X_2 was experimentally determined to be 138 parts by weight of gallium. Hence, as two atoms of aluminium were replaced by 138 unit masses of gallium without change of crystalline form, and as the aluminium and gallium compounds were very similar in their chemical relations, the conclusion was drawn that 138 represents the relative weight of two atoms of gallium; therefore the value $\frac{138}{2} = 69$ was deduced for the atomic weight of gallium. This number was afterwards confirmed by analyses of gaseous gallium chloride, and by determinations of the specific heat of the metal. It was at one time supposed by H. Rose (*P.* 108, 273) that a metal existed closely allied to, but not the same as, niobium; but Marignac (*A. Ch.* 60, 257) found that compounds obtained from this hypothetical metal were isomorphous with the corresponding compounds of tin and titanium, and that the groups of atoms SnF and TiF could be replaced by an atom of Rose's 'hyponiobium' without change of crystalline form. Hence Marignac suggested that 'hyponiobium' was a compound; and, because of various reactions, that it was a compound of niobium and oxygen in the proportion expressed by the formula NbO, where Nb has the value 94. If this were admitted it followed that the groups NbO, SnF, and TiF, were crystallographically equivalent in various compounds; but if so, it also followed, from analyses of the various compounds, that one atom of tin (=117·8 parts by weight), and one atom of titanium (=48 parts by weight), were replaced by 94 parts by weight of niobium in isomorphous compounds; therefore the atomic weight of niobium was 94. This value was confirmed by determinations of the relative densities, and by analyses, of the gaseous chloride and oxychloride of niobium. In this case the comparison of the crystalline forms of compounds led at once to a determination of the atomic weight of an element, to a proof of the non-existence of a hypothetical metal, and to the recognition that a body supposed to be an element was really a compound. An analogous case is furnished by Roscoe's researches on vanadium; in this case also the study of isomorphism led to the correct determination of the atomic weight of vanadium, and to the discovery that the body supposed to be vanadium was in reality a compound of this metal with oxygen (*T.* 1868. 1 *et seq.*).

No practical definition of the atomic weight of an element can be given in terms of the data of isomorphism. The foregoing examples serve to show how these data are applied to supplement those gained by the analyses of gaseous

compounds, and by determinations of the specific heats, of the elements.

If the atomic weight of calcium is known, then the isomorphism of the carbonates of Mg, Sr, Ba, Pb, Mn, Zn, and Fe, with the carbonate of calcium, helps to fix values for the atomic weights of these 7 elements; the isomorphism of the sulphates of Co, Ni, and Cu, with sulphate of iron gives data from which values may be deduced for the atomic weights of Co, Ni, and Cu; values are found for the atomic weights of Tl and Hg from considering compounds of these elements isomorphous with corresponding compounds of Pb; similarly, Zn and Cd—Fe, Al, and Cr—form many isomorphous compounds; many manganates are isomorphous with selenates and chromates, some chromates are isomorphous with molybdates and tungstates, permanganates are frequently isomorphous with perchlorates and periodates, hence values are found for the atomic weights of Se, Cr, Cl, and I, and also for Mo, and W; from copper we pass to silver through the isomorphism of Cu_2S and Ag_2S; silver leads on to sodium and the alkali metals on the one hand and to gold on the other hand; the compounds RS_2 and RAs_2 are isomorphous, hence conclusions can be drawn regarding the atomic weight of As, and from this the passage is easy to conclusions regarding the atomic weights of P, V, Sb, and Bi; iron is connected with Ti, and this with Si, Zr, Sn, and Th; lastly, given the atomic weight of Pt, Ir, Pd, Ro, Ru, or Os, values can be assigned to the other metals of this group from a study of the composition of isomorphous compounds of these metals. Thus it is seen how helpful is the study of isomorphism in determining the atomic weights of the elements.

These then are the three generally applicable methods whereby values may be found for the atomic weights of the elements: the method founded on the law of Avogadro; the method based on the study of the specific heats of solid elements; and the method which considers the relations between the chemical composition and the crystalline form of similar compounds. The first of these methods can be applied to determine the atomic and molecular weights of elements and the molecular weights of compounds, but the application is restricted to bodies which are gasifiable without decomposition; the second and third methods can be applied, strictly speaking, only to find values for the atomic weights of solid elements or of elements which form solid compounds.

All the methods are essentially physical; they are based on physical conceptions, and they are to a great extent developed by physical reasoning.

The conception of the molecule of a gaseous element or compound which is implied in the statement, 'equal volumes of gases contain equal numbers of molecules,' is wholly physical. The image of the molecule which this statement calls up in the mind is that of a small definite portion of matter 'which moves about as a whole so that its parts, if it has any, do not part company during the motion of agitation of the gas' (Clerk Maxwell). It is when this conception is applied to chemical changes that we are forced to admit that in many of these changes the parts of molecules do part company; thus we are led to the chemical conception of the atom, as a portion of matter smaller than the molecule, and either itself without parts, or else composed of parts which, so far as we know at present, do not part company during any of the changes which the atom undergoes. Then we proceed to study the properties of these atoms; and among these properties we seem to find two of great importance; the property namely which is expressed in the statement that the atoms of all solid elements, at certain temperatures, have equal capacities for heat; and the property which may be expressed in the statement that identity of crystalline form among compounds is usually accompanied by equality in the number of atoms of which the chemically reacting masses of these compounds are composed.

But here we ask: Are the *molecules* of isomorphous compounds built up of equal numbers of atoms? Can the physical conception of molecule, which has been gained by the study of gaseous phenomena, be applied to solid compounds? And the answer at present is: it is those small masses of isomorphous compounds which take part in chemical reactions, which as a rule, are composed of equal numbers of atoms. The physical definition of molecule cannot, in the present state of knowledge, be safely applied to solid and liquid bodies. Thus we seem to arrive at two conceptions, and two definitions, of the molecule. On the one side we have the physical conception, as that of a small mass of a gaseous element or compound which moves about as a whole, and the parts of which do not part company during the motion of agitation of the gas; and on the other side we have the chemical conception, as that of the smallest mass of an element or compound which takes part in a chemical change, and which exhibits the properties of the specified element or compound.

The first of these definitions holds good whether the small particles of a gas are themselves composed of smaller particles, or are chemically indivisible. The volume occupied by a number of gaseous molecules is independent of the numbers of atoms which by their union form these molecules: in one case a gaseous molecule may consist of a single atom (Hg and Cd), in another case a gaseous molecule may be formed by the union of 2 atoms (HCl), 3 atoms (H_2O), 9 atoms (C_2H_6O), 11 atoms ($C_3H_6O_2$), or a much larger number of atoms; but in every case, equal volumes of the gases contain equal numbers of molecules. But we know of no single property of liquid and solid compounds which is similarly independent of the number of atoms forming the atomic complex or reacting chemical unit of the compound.

Let us consider the conception of the chemically reacting unit or collocation of atoms a little more closely. We have already seen that the application of the empirical laws of chemical combination could not lead to final determinations of the atomic weights of elements, because these laws could not enable chemists to determine which of several values should be given to the smallest mass of a compound capable of exhibiting the properties of that compound. The value 8, 16, 24, &c. would be assigned to the atomic weight of oxygen, according as the

'atom' of water—that is, in Daltonian language, the smallest mass of water which exhibits the properties whereby water is distinguished from all other kinds of matter—was assumed to be 9, 18, 27, &c. times heavier than the atom of hydrogen. But a study of the properties of water leads to the conclusion that the 'atom' of water very probably contains two atoms of hydrogen and one of oxygen, and that the atomic weight of oxygen is therefore more probably represented by the number 16 than by the number 8. Thus, if 9 grams of water react with chlorine or bromine in sunlight 8 grams of oxygen are evolved, and 36·5 grams of a compound of hydrogen with chlorine, or 81 grams of a compound of hydrogen with bromine, are produced; in the former case, the 36·5 grams of the chlorine compound are proved by analysis to be composed of 35·5 grams of chlorine and 1 gram of hydrogen; in the latter case, the 81 grams of the bromine compound are proved to be composed of 80 grams of bromine and 1 gram of hydrogen; in both cases the whole of the oxygen of the 9 grams of water is removed from combination with the hydrogen and makes its appearance as free oxygen. Again, if 9 grams of water are acted on by potassium, ·5 grams of hydrogen are evolved, and 28 grams of a compound of potassium, hydrogen, and oxygen, containing 8 grams of oxygen—*i.e.* all the oxygen originally combined with hydrogen in the 9 grams of water—are at the same time produced; if these 28 grams of the new compound are dried, fused, and, while molten, are acted on by potassium, ·5 grams of hydrogen are evolved, and 47 grams of a new compound of potassium and oxygen are produced, which 47 grams contain the whole of the oxygen (*i.e.* 8 grams) originally combined with hydrogen in the 9 grams of water. These experiments prove that the hydrogen in a specified mass of water can be removed from that mass of water in two equal portions, but, so far as these experiments go, that the oxygen in the same mass of water is either not removed at all, or is wholly removed, from combination with hydrogen. Hence the conclusion is drawn that the smallest reacting mass of water contains one chemically indivisible mass of oxygen, but two chemically indivisible masses of hydrogen. But masses of hydrogen and oxygen are combined in water in the ratio 1:8; hence, if the smallest reacting mass of water is composed of 2 smallest parts, *i.e.* atoms of hydrogen, and one smallest part, *i.e.* atom, of oxygen, it follows that the atomic weight of oxygen is at least 16, that of hydrogen being unity, and that the relative mass of the smallest reacting portion, that is the *reacting weight*, of water is represented by the number 18, not by the number 9.

What value is to be assigned to the reacting weight of marsh gas? Masses of carbon and hydrogen combine to form marsh gas in the ratio 3:1; hence the value we are seeking cannot be less, but may be greater, than 4. If 4 grams of marsh gas are acted on by chlorine, a series of 4 compounds is produced; the first of these compounds contains chlorine and hydrogen combined with carbon, the masses of carbon and hydrogen being in the ratio 3: ·75; the second and third contain the same three elements, in the second the carbon and hydrogen are in the ratio 3: ·5, and in the third in the ratio 3: ·25; the fourth is a compound of the whole of the carbon originally combined with hydrogen in the 4 grams of marsh gas with chlorine, and contains no hydrogen. If now 4 grams of marsh gas are burnt in a plentiful supply of oxygen 11 grams of carbon dioxide are produced, or if the same mass of marsh gas is burnt in a limited supply of oxygen 7 grams of carbon monoxide are produced; in each case the oxide of carbon formed contains the whole of the carbon originally combined with hydrogen in the 4 grams of marsh gas used. No compound has yet been obtained from 4 grams of marsh gas containing a smaller mass of carbon than was originally present in the marsh gas, *i.e.* containing less than 3 grams of carbon. The conclusion drawn from these experiments is that the smallest mass of marsh gas which can take part in chemical changes is itself most probably composed of at least 4 atoms of hydrogen combined with at least one atom of carbon; but if this is granted it follows that an atom of carbon is 12 times heavier than an atom of hydrogen, and that the reacting weight of marsh gas is represented by a number certainly not smaller than 16.

We have thus determined, on chemical grounds and by chemical reasoning, the following values for the atomic weights of two elements: $(H=1)$ $C=12$, $O=16$. Now let us consider a compound of these elements. The simplest formula that can be given to acetic acid consistently with the values $H=1$, $C=12$, $O=16$, is CH_2O. If this acid is neutralised by soda, and the sodium salt so formed is analysed, this salt is found to be composed of the same masses of carbon and oxygen, combined with $\frac{3}{4}$ the mass of hydrogen, which were present in the mass of acid used; hence the smallest reacting mass of acetic acid must contain at least 4 atoms of hydrogen. But if this is granted it follows, from the fact that the elements are combined in the ratio $C:2H:O$, that this smallest reacting mass must also contain at least 2 atoms of carbon and 2 atoms of oxygen, and that the formula expressing the composition of the reacting weight of the acid in question must be written $C_2H_4O_2$. Further evidence in support of this conclusion is afforded by the preparation of thio-acetic acid, which is composed of carbon, hydrogen, oxygen, and sulphur, the carbon and hydrogen being present in the same ratio as in acetic acid, but the oxygen being present in the ratio of 16 to 4 hydrogen (*i.e.* $O:4H$), and the sulphur in the ratio 32 to 4 hydrogen. Now the atomic weight of sulphur is almost certainly 32; hence the simplest formula which expresses the composition of the reacting weight of thioacetic acid is C_2H_4OS. In this case, $\frac{1}{2}$ of the oxygen of the reacting weight of acetic acid is replaced by sulphur without any further change in the composition of the acid; hence, there must be at least 2 atoms of oxygen in the reacting weight in question, because atoms are (by definition) chemically indivisible.

This is an example of the general proposition that when $\frac{1}{n}$ of a constituent element of the reacting weight of a given compound can be replaced by another element without any other

change in the composition of the original substance, it follows that the reacting weight in question must contain at least *n* atoms of the element which has been removed; and that if the atomic weight of the replacing element is known, it is easy to calculate, from the composition of the original substance, the masses of the other constituents which must be present united with the *n* atoms of the specified element, and hence to assign a minimum value to the reacting weight of the original substance.

When a formula has been assigned to a compound by such chemical methods as those now sketched, it is frequently possible to argue from this to the formulæ of similar compounds. Thus, the properties and the methods of formation of sulphide of hydrogen show that this compound is similar to oxide of hydrogen (water); but if the reacting weight of water is represented by the formula H_2O, that of sulphuretted hydrogen is probably represented by the formula H_2S; again, the marked analogies between the sulphide, selenide, and telluride, of hydrogen suggest that these compounds have similar compositions; but if the first named is H_2S, the others are probably H_2Se, and H_2Te, respectively. If these formulæ are admitted, values are at once found for the atomic weights of the three elements, sulphur, selenion, and tellurium. Again, the metal magnesium reacts with water in the ratio of 24 parts by weight of the metal to 18 parts by weight of water, the products of this action being, (1) an oxide of magnesium containing 16 parts by weight of oxygen united with 24 parts by weight of magnesium, and (2) two parts by weight of hydrogen; hence, as the reacting weight of water is represented by the formula H_2O, that of magnesium oxide is probably represented by the formula MgO, where Mg = 24 parts by weight of magnesium; and hence the atomic weight of magnesium is probably 24.

The chemical methods for determining the atomic weights of elements then lead to a definition of atomic weight which may be stated thus: the atomic weight of an element is a number which tells how many times greater is the smallest mass of that element found in the chemically reacting weight of any of its compounds than the smallest mass of hydrogen found in the chemically reacting weight of any compound of hydrogen, such smallest mass of hydrogen being taken as unity. The difficulty in applying this definition lies in the vagueness of the expression 'the chemically reacting weight of a compound.' This expression cannot be defined; the illustrations already given indicate the interpretation usually put upon it, and also the methods whereby approximately accurate values are obtained for it in special cases.

The physical conception of molecule is clear, and admits of being put into words which have a definite quantitative meaning; this conception leads to that of the atom, the definition of which may also be put into a quantitative form. But the definition of the molecule is strictly applicable only to gases; hence arises the need of a subsidiary definition. We conceive chemical changes occurring among liquid and solid bodies as occurring among the smallest particles of these bodies which are capable of existing as wholes and of exhibiting the properties of the bodies in question. These smallest particles we may call the chemically reacting units, or the reacting weights, of the bodies; they are generally called molecules; but if we use this term we must not forget that it is employed in a somewhat vague manner, and without the strict quantitative signification which is attached to it when we speak of the molecule of a gas.

It seems probable that the mass of the chemically reacting unit of a compound varies, within certain not very wide limits, in different reactions. This mass must of course always be expressed by a whole multiple of a certain number; but it is probable that the value of the multiple varies. Thus many of the reactions of potassium permanganate can be simply expressed by assigning to the reacting weight of this salt the formula $KMnO_4$; but other reactions indicate that this formula should be doubled and written $K_2Mn_2O_8$. Again, periodic acid generally reacts as if the smallest particle which exhibits the chemical properties of this acid had the mass 228, and were composed of hydrogen, iodine, and oxygen, combined as shown in the formula H_5IO_6; but some of the reactions of periodic acid are more simply explained by doubling the formula, and writing it $H_{10}I_2O_{12}$. Indeed, even in the case of gaseous elements and compounds, we have sometimes direct evidence to show that the molecular weight of the gas varies with variations of temperature. Consider, for instance, the following data:—

SPEC. GRAV. OF IODINE GAS (Air = 1).

Pressure	Temperature	Sp. gr.
760 mm.	448°	8·74
,,	855	8·07
,,	1275 (approx.)	5·82
,,	1470 (approx.)	5·06
76 mm.	1250 (approx.)	4·72

SPEC. GRAV. OF SULPHUR GAS (Air = 1).

Pressure	Temperature	Sp. gr.
760 mm.	520°	6·62
,,	660	2·93
,,	860	2·23

(*cf.* SULPHUR, vol. iv.)

SPEC. GRAV. OF ACETIC ACID GAS (Air = 1).

Pressure	Temperature	Sp. gr.
760 mm.	124°	3·20
,,	130	3·11
,,	160	2·48
,,	230	2·09
,,	280	2·08
,,	338	2·08

SPEC. GRAV. OF NITROGEN TETROXIDE GAS (Air = 1).

Pressure	Temperature	Sp. gr.
125 mm.	−6°	3·01
138 ,,	+1	2·84
760 ,,	70	1·93
,, ,,	135	1·60
,, ,,	185	1·57

The density of iodine gas would be 8·77 if the composition of the molecule were represented by I_2, and 4·38 if the composition of the molecule were represented by I: the numbers given point to the existence of molecules having the composition I_2 at comparatively low

temperatures, and having the composition I at high temperatures when the gas is under a small pressure. The numbers given for sulphur gas suggest the existence of molecules S_8 at temperatures from b.p. to c. 550°, and of molecules S_2 from c. 650° to c. 1000°; but more recent results throw considerable doubt on the accuracy of this conclusion (*cf.* SULPHUR, vol. iv.) In the case of acetic acid gas, experiments indicate the existence of two different molecules; the data point to the existence of the molecules $C_2H_4O_2$ (calculated sp. gr. = 2·08, air = 1) at about 230° and upwards, but to the existence of heavier molecules, $C_3H_6O_3$ (calculated sp. gr. = 3·12, air = 1), at about 120°–130°. Lastly, the existence of the molecules N_2O_4 (calculated sp. gr. = 3·18) in gaseous nitrogen tetroxide at low temperatures and pressures, and of the molecules NO_2 (calculated sp. gr. = 1·59) at higher temperatures, is indicated by the numbers which represent the observed relative densities of this gas. The sp. gravs. of some gases slowly decrease as temperature rises until a value is attained which remains constant throughout a considerable interval, *e.g.* iodine, acetic acid, nitrogen tetroxide, gases; in other cases the sp. gr. remains nearly constant throughout a considerable range of temperature, and then rapidly decreases until another constant value is reached, which again remains constant for a considerable temperature-interval, *e.g.* sulphur gas (*v.* DISSOCIATION, also ALLOTROPY, and ISOMERISM). But in both classes of gases the data point to the existence, at different temperatures, of more or less stable molecules, the mass of the heavier of which is a whole multiple of that of the lighter.

The practical conclusions to be drawn from these facts are, that before the molecular weight of a gas can be regarded as satisfactorily determined, observations of the sp. gr. of that gas must be made throughout a considerable range of temperature; and that the number which represents the sp. gr. in question for such a range of temperature is to be taken as the basis for calculating the molecular weight of the gas, or it may be in some cases the numbers which represent the sp. gravs., each for a considerable temperature-interval, are to be used for finding the different molecular weights of the gas.

If then the mass of the molecule of a gas may have a different value, and therefore the molecule be composed of a different number of atoms, at a high than at a low temperature—and so far as data goes it seems that the mass of the molecule, if variable, is greater at temperatures near the condensation point than at temperatures far removed from this point—it is at least very probable that, if we carry over the conception of the molecule from gases to liquids and solids, we must be prepared to regard the mass of the molecule of a liquid or solid compound as considerably greater than that of the molecule of the same compound in the gaseous state. But, in practice, when we speak of the molecular weight of a liquid or solid compound we use the term molecular weight with a meaning different from that which we assign to it when we speak of the molecular weight of a gas. In the latter case the term signifies a small mass of matter, itself built up of smaller parts, which collides with other similar small masses, rebounds, vibrates, but yet remains intact, when a number of these small parts of matter are heated; in the former case the term summarises a number of chemical data in a convenient form, and asserts that the number of atoms which are so associated as to act in many changes as a chemical whole, is not less than a certain specified number.

The chemical formulæ of solid and liquid bodies do not then stand on the same footing as the formulæ of gases (*v.* FORMULÆ). But the question arises: are these collocations of atoms which we have called reacting chemical units also the reacting physical units of this or that compound? Are the physical constants of compounds conditioned by the masses of these reacting units? If these questions are answered in the affirmative, it is possible that measurements of some physical constant for a series of chemically similar compounds might enable just conclusions to be drawn regarding the relative masses of the reacting units of these compounds. Many measurements of this kind have been made; but no wide generalisation has yet been found which enables us to determine the relative masses of the reacting units of solid and liquid compounds from a knowledge of the physical constants of these compounds. All the generalisations which have been, or which at present can be, ventured upon, are for the most part empirical; the theory of the grained structure of matter has been developed, so far as it has been developed, only for gases; as regards gases, conclusions can be drawn from the fundamental principles of the theory, and these conclusions can be tested by experiment; but as regards liquids and solids, no such general conclusions can be drawn, and the theory can be used as a guide in experimental research only in a wide and general manner. What is wanted now is therefore not only further experimental determinations of the physical constants of series of chemically similar compounds, but a great development of the general theory of the structure of matter, especially in the direction of applying this theory to liquid and solid bodies (*v.* MOLECULAR THEORIES, also PHYSICAL METHODS). The great difficulty lies in the fact that most of the physical constants of liquid and solid compounds appear to be conditioned both by the nature and number, on the one hand, and by the modes of combination, on the other hand, of the atoms which form the atomic complexes we have called reacting chemical units. But the kinetic theory of gases has been chiefly developed from the study of properties which are independent of the nature and number, and are conditioned only by the states of union, of the parts of molecules.

But although we must for a time be content with the conception of the chemically reacting unit of a liquid or solid compound, and although we may at times wistfully contrast this with the clear physical conception of the molecule of a gas, yet there is one well-established chemical generalisation by the application of which values may be obtained for the atomic weights of many elements. This generalisation may be stated thus:—*The properties of the elements vary periodically with variations in the atomic*

weights of the elements; **or thus:—*If the elements are arranged in order of increasing atomic weights, the properties of the elements vary from element to element, but return more or less nearly to the same values at certain fixed points in the series.*** Let the elements be arranged in the order of their atomic weights, from hydrogen to uranium; let them be divided, broadly, into series of sevens; let the second series be placed under the first, the third under the second, and so on; then the elements contained in any one vertical column are called a *group*, and those in any one horizontal column are called a *series*. In this arrangement hydrogen is placed in a series by itself, and under it, that is in the same group, is placed the element (lithium) which comes next after hydrogen in order of increasing atomic weight; certain gaps are also supposed to occur in the list of elements, so that an element which immediately succeeds another in order of increasing atomic weights is sometimes placed, not in the group immediately succeeding, but in the group next but one or next but two &c. after, that which contains the element with the smaller atomic weight. Thus uranium (240) comes after thorium (232) in order of atomic weights; thorium is placed in group IV.; but uranium is placed in group VI. Certain elements are also placed in an eighth group by themselves; and the last member of each series in this group is repeated as the first member of the next series in group I.

The following table shows the arrangement of the elements in accordance with the *periodic law*. The formula at the head of each group represents the composition, either of the highest, or of the most characteristic, oxide of the elements belonging to that group; in each case the formula gives the number of atoms of oxygen referred to two atoms of the element.

parts, and to examine the nature of the connexion between the atomic weights, and such measureable properties, of the elements, as atomic volume

$$\left(i.e.\text{ the quotient }\frac{\text{atomic weight}}{\text{S.G. of solid element}}\right),$$

position in electrical series, fusibility, composition of oxides, chlorides, &c., wave lengths of characteristic lines in the spectra, heats of combustion or of combination with chlorine, &c. &c. The expression 'properties of the elements' is also to be taken as including the properties of the compounds of the elements; so that the periodic law asserts that *e.g.* the melting-points of similar compounds (say of chlorides) vary periodically with variations in the atomic weights of the elements.

The periodic law will be discussed in detail in the article with that heading; meanwhile suffice it to say that the law rests on a firm basis of well-established facts of diverse kinds. We shall here make use of this law to establish values for the atomic weights of one or two typical elements.

At the time of the publication of Mendeléeff's first memoir on the periodic law no elements were known which could be placed in group III. series 4 and 5. Calcium (40) and titanium (48) were known; zinc (65) and arsenic (75) were known: calcium and zinc evidently belong to the group which comprises magnesium, strontium, cadmium, and barium; titanium must be placed in the same group as carbon, silicon, and tin; and arsenic could not be separated from phosphorus, vanadium, and antimony. Hence two gaps occurred in group III. (series 4 and 5), and one in group IV. (series 5). From considering the difference between the values of the atomic weights of consecutive elements, (1) in

Series	GROUPS. I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	[R_2O_8]
1	H = 1	—	—	—	—	—	—	—
2	Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35·5	
4	K = 39	Ca = 10	Sc = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56 Ni = 58·6 Co = 59 Cu = 63
5	(Cu = 63)	Zn = 65	Ga = 69	Ge = 72	As = 75	Se = 79	Br = 80	
6	Rb = 85	Sr = 87	Y = 89	Zr = 90	Nb = 94	Mo = 96	(? 100)	Rh = 104 Ru = 104·5 Pd = 106 Ag = 108
7	(Ag = 108)	Cd = 112	In = 114	Sn = 118	Sb = 120	Te = 125	I = 127	
8	Cs = 133	Ba = 137	La = 139	Ce = 140	Di = 141	? 149	? 150	? 152—156 4 Elements ?
9	? 4 Elements 156 to 162 ?				Er = 166	? 167	? 169	
10	? 170	? 172	Yb = 173	? 178	Ta = 182	W = 184	? 190	Os = 191 Ir = 192·5 Pt = 194 Au = 197
11	(Au = 197)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	? 2 Elements 212 to 220 ?		
12	? 3 Elements 220 to 230 ?			Th = 232	? 237	U = 240	? 245	

In order to establish the existence of a periodic connexion between the atomic weights and the properties of the elements, it is necessary to break up the phenomena connoted by the phrase 'properties of the elements' into the same series the average value of this difference is about 2 in series 3, 4, and 5—and (2) in the same group—the average value of this difference for the first, second, and third members of groups I., II., and III., and for the first

and second members of groups IV., V., VI., and VII., is about 15, and for the succeeding members of these groups it is about 23—Mendeléeff assigned the value 44 as approximately that of the atomic weight of the unknown element in series 4 of group III., and the value 69 as approximately that of the atomic weight of the unknown element in series 5 of the same group. Mendeléeff also predicted many of the properties of these two unknown elements from considering the positions they occupied in the 'periodic' arrangement of the elements. Thus, the relations of the unknown element with atomic weight 44 to aluminium should be similar to those between (1) calcium and magnesium, (2) titanium and silicon, (3) vanadium and phosphorus, (4) chromium and sulphur; again the relations between (1) beryllium and calcium, (2) carbon and titanium, (3) nitrogen and vanadium, (4) oxygen and chromium, (5) fluorine and manganese, ought to be similar to the relations between boron and the unknown element. As regards the properties of the second unknown element with atomic weight 69, it was known that (1) zinc is more like magnesium than it is like calcium, (2) arsenic more resembles phosphorus than it does vanadium, (3) selenion shows closer analogies with sulphur than with chromium, and (4) bromine and chlorine are more like each other than either is like manganese; hence, it was argued, the unknown element (69) will resemble aluminium more closely than it resembles the other unknown element (44), and more closely than the second unknown element itself resembles aluminium. The relationships indicated were of course studied in detail by Mendeléeff. Thus, take the pairs of consecutive elements in series 3 and 4; the resemblance between any of these pairs (Na, K; Mg, Ca; Si, Ti; P, V; S, Cr; Cl, Mn) is less marked in the higher than in the lower groups. Or, take the two elements in each group belonging respectively to series 3 and 5; the resemblance between any of these pairs (Na, Cu; Mg, Zn; . . . P, As; S, Se; Cl, Br) is more marked in the higher than in the lower groups.

The relationships examined by Mendeléeff were those between atomic weights, fusibilities, atomic volumes, composition of oxides chlorides and other compounds, acid or basic character of oxides, power of forming double salts and composition of these salts if formed, &c. &c. As a result of his study of these relationships, Mendeléeff tabulated many properties of the two unknown elements. Since the memoir of the Russian naturalist was published, several new elements have been discovered; some of the properties of two of these elements will now be compared with the properties which Mendeléef asserted ought to characterise the elements belonging respectively to series 4 and 5 of group III.

Mendeléeff's Eka-aluminium (III.-5).

Atomic weight about 69.
Readily obtained by reduction.
Melting-point low. Sp. gr. = 5·9.
Not acted on by air.
Will decompose water at a red heat.
Slowly attacked by acids or alkalis.
Will form a potassium alum more soluble, but less easily crystallisable, than the corresponding aluminium salt.
Oxide = El_2O_3. Chloride = El_2Cl_6.

Gallium.

Atomic weight = 69.
Readily obtained by electrolysing alkaline solutions.
M.P. = 30·15°. Sp. gr. = 5·93.
Non-volatile, and but superficially oxidised in air at bright red heat.
Decomposes water at high temperatures. Soluble in hot hydrochloric acid, scarcely attacked by cold nitric acid; soluble in caustic potash.
Forms a well-defined alum.
Chloride = Ga_2Cl_6. Oxide = Ga_2O_3.

Mendeléeff's Eka-boron (III.-4).

Atomic weight about 44.
Oxide Eb_2O_3 soluble in acids; sp. gr. about 3·5; analogous to but more basic than Al_2O_3; less basic than MgO; insoluble in alkalis.
Salts of Eb colourless, and will yield gelatinous precipitates with KOH, K_2CO_3, Na_2HPO_4, &c.
Sulphate, $Eb_2.3SO_4$, will form a double salt with K_2SO_4, probably not isomorphous with the alums.
Chloride $EbCl_3$ or Eb_2Cl_6, sp. gr. about 2, less volatile than Al_2Cl_6.

Scandium.

Atomic weight = 44.
Oxide Sc_2O_3; sp. gr. = 3·8; soluble in strong acids; analogous with but more decidedly basic than Al_2O_3; insoluble in alkalis.
Solutions of Sc salts colourless and yield gelatinous precipitates with KOH, K_2CO_3, and Na_2HPO_4.
Sulphate, $Sc_2.3SO_4$, forms a double salt, not an alum, $Sc_2 3SO_4.3K_2SO_4$.

Gallium and scandium are, therefore, the elements which Mendeléeff named *eka-aluminium* and *eka-boron*, and many properties of which were accurately and in detail tabulated by him, while the elements were yet unknown.

Much discussion has of late been carried on, and a great deal of experimental work has been done, regarding the value to be given to the atomic weight of beryllium. Chemists are agreed that the value in question is either (in round numbers) 9 or $9 \times 1\frac{1}{2} = 13·5$; if the former value is adopted, beryllium must be placed in group II. series 2; if the latter value is preferred, the metal must find a place between carbon and nitrogen. If the former value is adopted, the formula of beryllium oxide becomes BeO; if the latter value is preferred, the formula of this oxide must be written Be_2O_3. The periodic law is a guide in the solution of this problem. Briefly, the law directs us to study the properties of the element itself and the composition and properties of its compounds; to compare these with those of elements which must come in the same group and the same series as beryllium; to compare the relations between beryllium and these other elements with the relations which have been established between elements occurring in positions similar to that occupied by beryllium and the other elements in question; and to adopt

that value for the atomic weight of beryllium which best harmonises with the outcome of this study. There can be no doubt that the value which best harmonises with the results of this study is 9; hence the atomic weight of beryllium is almost certainly 9. This result is confirmed by the application of the law of Dulong and Petit, and also of the law of Avogadro; for the specific heat of beryllium at about 500° is nearly constant and is approximately represented by the number ·62 (·62 × 9 = 5·6), and the vapour-densities of beryllium chloride and bromide show that the formulæ of these compounds, as gases, are $BeCl_2$, and $BeBr_2$, respectively (Be = 9).

The atomic weight of tellurium had for long been supposed to be greater than that of iodine (127); but if this were so tellurium must be placed in group I. series 9; that is to say, in a group which contains the alkali metals. This position cannot be defended; moreover, every chemist knows that tellurium exhibits marked analogies to sulphur and selenion. But if tellurium is to find a place in group VI. the value to be given to its atomic weight must be greater than 120 and less than 127. In 1883 Brauner undertook an experimental criticism of the methods whereby the atomic weight of tellurium had been determined by different chemists. Brauner proved that these methods almost necessarily gave too large values; he also made very careful determinations of the atomic weight of the element by two new methods, and obtained a series of numbers varying from 124·94 to 125·4, with a mean value of 125. The periodic law has, therefore, prevented chemists from finally adopting an erroneous value for the atomic weight of tellurium, notwithstanding the great weight of authority which was in favour of regarding that value as correct.

These examples will suffice to show how the periodic law is used as a guide in determining what multiple of the combining weight of an element is to be adopted as the atomic weight of that element. Incidentally, these examples also impress us with the extreme importance of the constants which we call the atomic weights of the elements. Given this constant for a new element, and we may, to a considerable extent, predict the properties of the element and its compounds. The periodic law also enables values to be given, if not to the molecular weights, then certainly to the reacting weights of compounds; because the position of an element in a group and series determines the formulæ of the salts of that element, and, as we assume the atomic weights of the other elements in these salts to be known, therefore determines the relative masses of the chemically reacting units of these salts. There are at least one or two elements in each group which form some gasifiable compounds; the molecular weights of these compounds are therefore known; hence conclusions may tentatively be drawn regarding the molecular weights of similar compounds of other elements in the same group. But no great stress must be placed on such reasoning as this. Aluminium and indium occur in group III. (series 3 and 7), these metals exhibit fairly marked analogies; yet the molecular formula of gaseous aluminium chloride is Al_2Cl_6 while that of gaseous indium chloride is $InCl_3$; thallium belongs to the same group as aluminium and indium (series 11), yet the formula of the only chloride of thallium which is stable as a gas is TlCl.

There is then at present one generally applicable method for determining the molecular weights of gaseous elements and compounds; this method springs out of the application of the generalisation of Avogadro to chemical changes occurring between gaseous elements. The application of the generalisation in question leads to practical definitions of the terms molecular weight and atomic weight. In addition to this method there are three others which serve to determine, more or less accurately, the values of the atomic weights of the elements; and two of these are also employed to find the relative masses of the small particles of solid and liquid compounds which take part in chemical changes.

The methods founded respectively on the laws of Avogadro, Dulong and Petit, and Mitscherlich, are essentially physical methods; they are outcomes of the physical theory of the grained structure of matter. The applications of this theory to chemical phenomena which have been considered in the present article have been treated in a purely empirical manner. But it is possible to deduce the law of Avogadro from the first principles of the theory in question. The theory assumes that the temperature of a gas represents the mean kinetic energy of the molecules of that gas; hence, if M and M_1 represent the masses, and V^2 and V_1^2 the mean squares of the velocities, of the molecules of two gases at the same temperature, it follows, from the laws of energy, that

$$MV^2 = M_1V_1^2.$$

But if the pressures of the two gases are equal, then

$$MNV^2 = M_1N_1V_1^2;$$

where N and N_1 represent the number of molecules in unit volume of the two gases; because, according to the theory, the pressure of a gas on the walls of the containing vessel is an effect of the impacts of the molecules of the gas, and this depends on the number and velocity per unit of time of these molecules. From these equations it follows that

$$N = N_1;$$

that is, when two gases are at the same pressure and temperature the number of molecules in unit volume of either gas is the same. But this is the law of Avogadro.

Neither the law of Dulong and Petit, nor the law of isomorphism, can as yet be satisfactorily deduced from the first principles of the molecular theory. We know very little, if anything, of the structure of gaseous molecules; and of the molecular phenomena of solids our accurate knowledge may be said to be almost nothing (*v.* AGGREGATION, STATES OF, p. 87; also MOLECULAR STRUCTURE OF MATTER, THEORIES REGARDING; also PHYSICAL METHODS APPLIED TO CHEMICAL PHENOMENA).

The atomic weights of all the known elements have been more or less accurately determined; but only fourteen elements have been gasified, and hence the molecular weights of only fourteen elements have been determined. The molecules of the greater number, but by no means of all,

these elements are *most probably* (*v.* remarks on 840 regarding the molecules of hydrogen, &c.) mposed of two atoms; they are diatomic. he following table shows the classification of the elementary molecules, so far as the available data permit, in accordance with their atomicity, that is, the number of atoms of which each molecule is composed.

Atomicity of Elementary Molecules (the temperatures are approximate).

Monatomic	*Diatomic*	*Triatomic*	*Tetratomic*	*Hexatomic*
odium otassium inc admium Iercury odine at c. 1500° Bromine at c. 1800°) ntimony at c. 1700°	Hydrogen Chlorine Bromine Iodine at 200°–1000° Oxygen Sulphur at 800° and upwards Selenion at 1200° and upwards Tellurium Nitrogen Phosphorus } at white heat Arsenic }	Oxygen as ozone Selenion at 700°–800°	Phosphorus Arsenic (both at temps. nearly up to white heat)	Sulphur at 450–550° (very doubtful; *v.* Biltz a. Meyer, *B.* 21, 2013)

The following table presents the data available for calculating the molecular weights of the lementary gases:—

Molecular Weights of Elementary Gases.

I. Name of element	II. Relative density air=1	III. Temp. of observation	IV. Density ×28·87	V. Molecular weight	I. Name of element	II. Relative density air=1	III. Temp. of observation	IV. Density ×28·87	V. Molecular weight
[1] Hydrogen	·06926	0°	2	2	[17] Bromine	5·54	100°	159·9	159·5
[1a] Sodium	·87	1200°–1500°	25·5	23	[18] ,,	5·38	100°	155·3	
[2] Nitrogen	0·9713	0°	28·04	28·02	[19] ,,	4·43	abt. 1500°	117·9	?
[3] Oxygen	1·106	abt. 1400°	31·94	31·92	[20] Selenion	5·68	abt. 1400°	161·1	157·6
[4] ,,	1·10563	0°	31·92		[21] ,,	6·37	abt. 1000°	183·9	?
[5] ,, (ozone)	1·658	—	47·86	47·88	[22] ,,	7·67	860°	221·4	236·4
[6] Sulphur	2·23	860°	64·4	63·96	[23] Mercury	6·96	abt. 1000°	200·93	199·8
[7] ,,	2·24	1040°	64·6		[24] ,,	6·98	446°	201·5	
[8] ,,	2·17	abt. 1400°	62·6		[25] ,,	7·03	424°	203·0	
[9] Zinc	2·38	abt. 1400°	68·7	64·9	[26] ,,	6·7	882°	193·4	
[10] Chlorine	2·45	200°	70·73	70·71	[27] Iodine	8·8	250°–150°	254·0	253·01
[11] ,,	2·61	abt. 1000°	75·35		[28] ,,	8·72	185°	251·7	
[11a] ,,	2·44	abt. 1200°	70·72		[29] ,,	8·70	447°	251·2	
[12] Cadmium	3·94	abt. 1000°	113·7	112·1	[30] ,,	8·72	abt. 1000°	251·7	
[12a] Antimony	9·78	1640°	136·1	120	[31] ,,	8·84	250°	255·2	
[13] Phosphorus	4·35	500°	125·6	123·84	[31a] ,,	8·55	665°	246·8	
[14] ,,	4·50	abt. 1000°	129·9		[32] ,,	5·87	abt. 1100°	169·4	?
[15] Arsenic	10·2	860°	294·5	299·6	[33] ,,	4·76	abt. 1500°	137·4	[? 126·58]
[16] ,,	10·65	644°–668°	307·4		[34] Tellurium	9·08	abt. 1400°	262·1	255
[16a] ,,	6·53	1430°	188·5	[?149·8]					

[1] Regnault, *C. R.* 20, 975. [1a] Scott, *Pr. E.* 14, 410.
[2] Regnault, *l.c.* [3] V. Meyer, *B.* 12, 1126.
[4] Regnault, *l.c.* [5] Soret, *C. R.* 61, 941; 64, 904.
[6, 7] Deville a. Troost, *C. R.* 56, 891.
[8] V. Meyer, *B.* 12, 1112.
[9] Mensching a. Meyer, *B.* 19, 3295.
[10] Ludwig, *B.* 1, 232. [11] V. Meyer, *B.* 13, 400.
[11a] Id. *B.* 15, 2773 (mean of 5 experiments).
[12] Deville a. Troost, *C. R.* 49, 239.
[12a] Biltz a. Meyer, *Z. P. C.* 4, 249.
[13, 14] D. a. T. *C. R.* 56, 891. [15] Id. *l.c.*
[16] Mitscherlich, *A.* 12, 159.
[16a] Biltz a. Meyer, *Z. P. C.* 4, 249.
[17] Mitscherlich, *l.c.* [18] V. Meyer, *B.* 13, 406.
[19] Crafts, *C. R.* 90, 183. [20, 21, 22] Deville a. Troost, *l.c.*
[23] V. Meyer, *B.* 13, 1107, 1110 (mean of 6 experiments).
[24] Dumas, *A. Ch.* [2] 33, 337. [25] Mitscherlich, *l.c.*
[26] Bineau, *C. R.* 49, 799.
[27] V. Meyer; a. Meier a. Crafts, *B.* 13, 868 (mean of 7 experiments).
[28] Dumas, *l.c.* [29, 30] Deville a. Troost, *l.c.*
[31] V. Meyer, *B.* 13, 396. [31a] Troost, *C. R.* 95, 30.
[32] V. Meyer, *B.* 13, 1115. [33] Id. 13, 1010.
[34] Deville a. Troost, *l.c.*

Biltz a. Meyer (*Z. P. C.* 4, 249) have obtained values which point to a mol. w. for phosphorus between P_4 and P_2, for bismuth between Bi_2 and Bi, and for thallium as Tl, at very high temperatures.

The following table presents a summary of the atomic weights of the elements and of the evidence upon which each value is based:—

ATOMIC WEIGHTS OF THE ELEMENTS.

I. Element	II. Principal compounds vapour densities of which have been determined	III. Specific heat: how determined	IV. Isomorphism: compounds compared [see Note A, p. 361]	V. Atomic Weight (1) By vapour density method	V. Atomic Weight (2) By sp. heat method	VI. Compounds analysed &c. in order to find combining weight of the element [see Note B, p. 361]	VII. Combining weight [Note B, p. 361]	VIII. Remarks [see Note C, p. 361]
Hydrogen	HF, HCl, HBr, HI, H_2S, H_2Se, H_2Te, H_3N, H_3P, H_4C, &c.	Indirectly [from sp. heat of H_2O, NH_4Cl, NH_4NO_3]. [Atomic heat abnormal?]	—	1				
Lithium	None	Directly	Li compounds with analogous compounds of alkali metals	—	7·01	[1] Lithium chloride	7·01	
Beryllium	$BeCl_2$, $BeBr_2$	Directly: sp. heat varies much with temperature	A few Be compounds with analogous compounds of Cd and Zn	9·08	9·08	[2] Beryllium sulphate	4·54	
Boron	BF_3, BCl_3, BBr_3, $B(CH_3)_3$	Directly: sp. heat varies much with temperature	—	10·9	10·9	[3] Borax; boron chloride	3·66	
Carbon	CH_4, CH_3F, CH_3Cl, CH_3Br, CH_3I, $CHCl_3$, CO, CO_2, $COCl_2$, COS, CS_2, CHN, C_2H_4O, $C_4H_{10}O$, &c	Directly: sp. heat varies much with temperature	CN compounds with those of F, Cl, Br, and I	11·97	11·97	[4] Diamond burnt to CO_2	2·99	
Nitrogen	NH_3, NO, NO_2, NOCl, N_2O, N_2O_4, &c.	Indirectly: very undecided [from sp. heats of various compounds]	NH_4 compounds with those of alkali metals	14·01	—	[5] Ammonium chloride; silver nitrate	4·67	
Oxygen	OH_2, ON_2, OC, OCl_2P, O_2C, O_2S, O_4Os, &c.	Indirectly: very undecided [from sp. heats of various compounds]	—	15·96	—	[6] Synthesis of water	7·98	
Fluorine	FH, $F(CH_3)$, F_3B, F_4Si, F_3P, &c.	Indirectly: very undecided [from sp. heat of CaF_2, &c.]	Metallic fluorides with analogous compounds of Cl, Br, and I	19·1	—	[7] Sodium fluoride; potassium fluoride; calcium fluoride	19·1	
Sodium	None	Directly	Na compounds with those of other alkali metals	—	23	[8] Sodium chloride	23	
Magnesium	"	"	Mg compounds generally with those of Zn, Mn, and Fe (in ferrous salts)	—	24	[9] Magnesium sulphate, do. chloride	12	
Aluminium	$AlCl_3$	"	With Cr, Mn, and Fe in R_2O_3 and derivatives	27·02	27·02	[10] Ammonia - alum; aluminium bromide; solution of aluminium in soda	9·007	

[1] **Li.** J. W. Mallet, *Am. S.* [2] 22, 349. Stas, *Nouvelles Recherches*, 368 and 274.
[2] **Be.** Nilson and Pettersson, *B.* 13, 1451.
[3] **B.** Berzelius, *P.* 2, 129. Deville, *A. Ch.* [3] 55, 180.
[4] **C.** Dumas and Stas, *A. Ch.* [3] 1, 5. Erdmann and Marchand, *J. pr.* 23, 159. Roscoe, *C. R.* 94, 1180.

[5] **N.** Stas, *Rapports*, 50, 87, 92, and *Nouvelles Recherches*, 57, 281.
[6] **O.** Erdmann and Marchand *J. pr.* 26, 468. Dumas, *A. Ch.* [3] 8, 189.
[7] **F.** Louyet, *A. Ch.* [3] 25, 291, 301. Dumas, *A. Ch.* [3] 55, 170. De Luca, *C. R.* 51, 291.

[8] **Na.** Pelouze, *C. R.* 20, 1047. Dumas, *A. Ch.* [3] 55, 182. Stas, *Rapports*, 78, and *Nouvelles Recherches*, 248.
[9] **Mg.** Jacquelain, *C. R.* 30, 106, and *A. Ch.* [3] 32, 202. Bahr, *J. pr.* 56, 310. Dumas, *A. Ch.* [3] 55, 189.
[10] **Al.** J. W. Mallet, *T.* 1880. 1003 *et seq.*

I. Element	II. Principal compounds vapour densities of which have been determined	III. Specific heat: how determined	IV. Isomorphism: compounds compared [see Note A, p. 361]	V. Atomic Weight (1) By vapour density method	V. Atomic Weight (2) By sp. heat method	VI. Compounds analysed &c. in order to find combining weight of the element [see Note B, p. 361]	VII. Combining weight [Note B, p. 361]	VIII. Remarks [see Note C, p. 361]
Silicon . . .	SiF_4, $SiCl_4$, SiI_4, $Si(CH_3)_4$, SiH_3Cl, Si_2OCl_6, $Si_2O(C_2H_5)_6$ &c.	Directly: sp. heat varies much with temperature ?	With C, Ti, Zr, Sn, and Th in compounds of type RO_2	28·3	28·3	[11] Silicon chloride and bromide	7	
Phosphorus .	PH_3, PCl_3, PI_3, PF_3, $POCl_3$, $PSCl_3$, P_2I_4, P_2H_4, $P_3N_3Cl_6$, &c.	Directly	Phosphates with vanadates and arsenates; organic compounds of P with those of N, As, and Sb	30·96	30·96	[12] Phosphorous chloride; synthesis of phosphorus pentoxide	10·32	
Sulphur . . .	SH_2, SO_2, SO_3, $SOCl_2$, S_2C, S_2Cl_2, &c.	"	With Se compounds; with Te compounds of type R″Te. Salts of H_2SO_4 with those of H_2CrO_4 and H_2TeO_4	31·98	31·98	[13] Synthesis of silver sulphide; reduction of silver sulphate by hydrogen	15·99	
Chlorine . .	ClH, $Cl(CH_3)$, $ClTl$, Cl_2Zn, Cl_2Hg, Cl_2HO, Cl_3Bi, Cl_3Sb, Cl_2O, Cl_4Si, Cl_4U, Cl_5Ta, Cl_5Mo, Cl_6W, &c.	Indirectly: doubtful [from comparison of various haloid compounds]	Chlorides, with analogous compounds of Br and I	35·37	—	[14] Potassium chlorate; synthesis of silver chloride		
Potassium . .	KI	Directly	K compounds with those of other alkali metals	39·04	39·04	[15] Potassium chloride, do. bromide	39·04	
Calcium . . .	None	"	Ca compounds with those of Sr, Ba, and in some cases Pb	—	39·9	[16] Calcium chloride; calcium carbonate	19·95	
Scandium . .	"	Sp. heats of some compounds determined	(? Sc compounds with those of other earth metals)	—	—	[17] Synthesis of scandium sulphate	14·66	*Sc.* **The atomic weight of this metal is most probably 14·66 × 3 = 44; if this is so, the oxide is Sc_2O_3, and is analogous with the oxides of the earth metals**
Titanium . .	$TiCl_4$	Directly	TiO_2 and some derivatives with analogous compounds of C, Si, Zr, Sn, and Th	48	48	[18] Titanium chloride and bromide	12	
Vanadium . .	VCl_4, $VOCl_3$	Sp. heats of one or two compounds determined	Vanadates with phosphates and arsenates	51·2	—	[19] Vanadium pentoxide, do. oxychloride	17·07	
Chromium . .	CrO_2Cl_2, $CrCl_2$, $CrCl_3$	Directly: (? too low)	Salts of H_2CrO_4 with those of H_2MnO_4 and H_2TeO_4; Cr_2O_3 with Al_2O_3, Mn_2O_3 and Fe_2O_3	52·4	52·4	[20] Chromium chloride; silver chromate. Potassium dichromate	26·2	
Manganese .	$MnCl_2$	" (? too high)	Mn_2O_3 with Al_2O_3, Cr_2O_3, and Fe_2O_3. R_2MnO_4 with R_2CrO_4 and R_2TeO_4. $RMnO_4$ with $RClO_4$	55	55	[21] Manganese chloride; manganoso-manganic oxide; manganous oxalate. Silver permanganate	27·5	
Iron	$FeCl_2$, $FeCl_3$	Directly	Fe_2O_3 and derivatives with Al_2O_3, Cr_2O_3, Mn_2O_3, and derivatives. Some Fe salts with those of Ni, Co, and Cu	55·9	55·9	[22] Synthesis of ferric oxide; reduction of ferric oxide; analysis of ferrous and ferric chlorides	27·95	

Nickel . . .	$Ni(CO)_4$	Directly	Ni with Co compounds: some Ni compounds with those of Fe (ferrous salts)	—	58·6	[23] Nickel chloride; nickelous oxide; strychnine-nickel cyanide; brucine-nickel cyanide	29·3
Cobalt . . .	„	„	Co with Ni compounds: some Co compounds with those of iron (ferrous salts)	—	59	[24] Ammonium-cobalt cyanide; phenyl-ammonium-cobalt cyanide; strychnine- and brucine-cobalt cyanides	29·5
Copper . . .	Cu_2Cl_2	„	Most Cu compounds with those of Ni and Co; some with Fe (ferrous) compounds. Cu and Ag compounds of type R_2O	63·2	63·2	[25] Reduction of copper oxide; electrolysis of copper sulphate	63·2
Zinc	$ZnCl_2$, $Zn(CH_3)_2$, $Zn(C_2H_5)_2$	„	Zn compounds with those of Mg and Mn	64·9	64·9	[26] Synthesis of zinc oxide	32·45
				65·48	65·48	[26a] Solution of zinc in dilute sulphuric acid	32·74
Gallium . . .	Ga_2Cl_6, $GaCl_3$, $GaCl_2$	Directly [? too low]	Ga-alum with other alums	69·9	69·9	[27] Oxidation of the metal; gallium-ammonia alum	23·3
Germanium .	$GeBr_4$, $GeCl_4$, GeS	Directly	—	72·32	72·32	[27a] Germanium tetra-chloride	18·08
Arsenic . . .	AsH_3, $AsCl_3$,* AsI_3, $As(CH_3)_2Cl$, As_4O_6, &c.	„	As compounds with those of Sb and Bi; organic compounds of As with those of N, P, and Sb: arsenates with phosphates and vanadates	74·9	74·9	[28] Arsenic bromide; do. chloride, do. oxide	24·97
Selenion . .	SeH_2, SeO_2, $SeCl_4$, $SeCl_2Br$	„	Se with S compounds	78·8	78·8	[29] Reduction of selenion dioxide; reduction of silver selenite	39·4
Bromine . .	BrH, $Br(CH_3)$, Br_2Cd, Br_3B, Br_4Sn, Br_4U, &c.	„	Bromides, with analogous compounds of Cl and I	79·75	79·75	[30] Synthesis of silver bromide; potassium bromide	79·75
Rubidium . .	RbCl, RbI	Indirectly: doubtful [from comparison of some compounds with those of other alkali metals]	Rb compounds with those of other alkali metals	85·2	—	[31] Rubidium chloride	85·2

[11] **Si.** Pelouze, *C. R.* 20, 1047. Dumas, *A. Ch.* [3] 55, 183. J. Schiel, *A.* 120, 94. Thorpe a. Young, *C. J.* 51, 576.
[12] **P.** Pelouze, *C. R.* 20, 1047. Schrötter, *A. Ch.* [3] 38, 131. Dumas, *A. Ch.* [3] 55, 174.
[13] **S.** Stas, *Rapports.* 53.
[14] **Cl.** Stas, *Rapports*, 38, 42, 44, 118, and *Nouvelles Recherches*, 208.
[15] **K.** Stas, *Rapports*, 69, 91, 118, and *Nouvelles Recherches*, 244.
[16] **Ca.** Berzelius, *P.* 8, 189. Dumas, *A. Ch.* [3] 55, 190. Erdmann and Marchand, *A.* 44, 216; 52, 210; 76, 219. Salvétat, *C. R.* 17, 318.
[17] **Sc.** Nilson, *B.* 13, 1439.
[18] **Ti.** H. Rose, *P. A.* 15, 145. J. Pierre, *A. Ch.* [3] 20, 507. Thorpe, *C. J.* 47, 108.
[19] **V.** Roscoe, *T.* 1868, 8, 23.
[20] **Cr.** E. Peligot, *A. Ch.* [3] 12, 530. Berlin, *A.* 56, 207; 60, 183. F. Kessler, *P.* 95, 210. Siewert, *Zeitschrift für die gesammten Naturwissenschaften*, 17, 530.
[21] **Mn.** Dumas, *A. Ch.* [3] 55, 151. Rawack, *P.* 107, 605. Schneider, *A.* 113, 79. Dewar and Scott, *Pr.* 35, 44.
[22] **Fe.** Berzelius, *A.* 50, 432. Svanberg and Norbin, *A.* 50, 432. Erdmann and Marchand, *A.* 52, 212. L. E. Rivot, *A.* 78, 214. Dumas, *A. Ch.* [3] 55, 157.
[23] **Ni.** Dumas, *A. Ch.* [3] 55, 149. Russell, *C. J.* [2] 1, 51. Somaruga, *Fr.* 6, 347. R. H. Lee, *B.* 4, 789.
[24] **Co.** Weselsky, *B.* 2, 592. R. H. Lee, *B.* 4, 789.
[25] **Cu.** Berzelius, *P.* 8, 182. Erdmann and Marchand, *P. C.*, 31. 391. W. Hampe, *Fr.* 13, 352. Baubigny, *C. R.* 97, 906.
[26] **Zn.** Gay-Lussac and Thenard, *G. A.* 37, 460. Berzelius, *P.* 8, 184. Erdmann, Berzelius's *Lehrbuch* (5th ed.), 3, 1219. P. A. Favre, *A. Ch.* [3] 10, 163. Marignac, *Ar. Sc.* [3] 10, 5, 193.
[26a] **Zn.** Reynolds and Ramsay, *C. J. Proc.* 1886–87. 81.
[27] **Ga.** Lecoq de Boisbaudran, *C. R.* 86, 941.
[27a] **Ge.** Winkler, *J. pr.* 1886, 177.
[28] **As.** W. Wallace, *P. M.* [4] 18, 379. Dumas, *A. Ch.* [3] 55, 174. F. Kessler, *P.* 95, 204.
[29] **Se.** Pettersson and Ekman, *B.* 9, 1210.
[30] **Br.** Stas, *Nouvelles Recherches*, 158, 170 and 18[illegible].
[31] **Rb.** Bunsen, *P.* 113, 339. Piccard, *J. pr.* 86, 45[illegible]. Godeffroy, *A.* 181, 189.

I. Element	II. Principal compounds vapour densities of which have been determined	III. Specific heat: how determined	IV. Isomorphism: compounds compared [see Note A, p. 361]	V. Atomic Weight (1) By vapour density method	V. Atomic Weight (2) By sp. heat method	VI. Compounds analysed &c. in order to find combining weight of the element [see Note B, p. 361]	VII. Combining weight [Note B, p. 361]	VIII. Remarks [see Note C, p. 361]
Strontium . .	None	Indirectly: doubtful [comparison of compounds of Sr, Ca, and Ba]	Sr compounds with those of Ca and Ba, and with some Pb salts	—	—	[32] Strontium chloride	43·65	*Sr.* The atomic weight of strontium must be taken as $43·65 \times 2 = 87·3$ if the formulæ of the salts are to become analogous to those of the Ba and Ca salts *Yt.* Atomic weight probably $= 29·87 \times 3 = 89·6$ because of analogy of Yt salts with those of the earth metals
Yttrium . . .	„	Sp. heats of a few compounds determined	Yt compounds with those of other earth metals	—	—	[33] Synthesis of yttrium sulphate	29·87	
Zirconium . .	$ZrCl_4$	Directly [? too low]	ZrO_2 with TiO_2, ThO_2, SnO_2, and SiO_2	90	90	[34] Zirconium chloride; potassium - zirconium fluoride	45	
Niobium . .	$NbCl_5$, $NbOCl_3$	—	Nb with Ta compounds. Nb fluorides and oxyfluorides with Mo do. do.	94	—	[35] Niobium chloride; potassium - niobium oxyfluoride	31·33	
Molybdenum	$MoCl_5$	Directly [? too high]	Mo with W compounds; some salts of H_2MoO_4 with those of H_2CrO_4. Mo with Nb fluorides and oxyfluorides	95·8	95·8	[36] Molybdenum dichloride, tetrachloride, and pentachloride	19·16	
Ruthenium .	RuO_4	Directly	Most Ru compounds with those of Rh, Pd, Ir, Pt, and Os	101·4	101·4	[37] Potassium-ruthenium chloride, &c.	25·35	
Rhodium . .	None	„	Most Rh compounds with those of Ru, Pd, Ir, Pt, and Os	—	102·7	[38] Potassium - rhodium chloride	25·55	
Palladium . .	„	„	Most Pd compounds with those of Ru, Rh, Ir, It, and Os	—	106·3	[39] Palladium chloride	26·58	
Silver	AgCl	„	Some Ag compounds with those of Na and other alkali metals. Ag with Cu compounds of type R_2O. A few Ag and Au compounds	107·66	107·66	[40] Silver chlorate, bromate, iodate: synthesis of silver bromide and iodide	107·66	
Cadmium . .	$CdBr_2$	„	Some Cd compounds with those of Be and Zn	112	112	[41] Cadmium bromide	56	
Indium . . .	$InCl_3$, $InCl_2$, InCl	„	Some In compounds with those of Cd and Be	113·4	113·4	[42] Synthesis of indium oxide	37·8	
Tin	$SnCl_2$, Sn_2Cl_4, $SnCl_4$	„	SnO_2 with TiO_2, ZrO_2, and ThO_2	117·8	117·8	[43] Synthesis of stannic oxide	58·9	
Antimony . .	$SbCl_3$, $SbBr_3$, SbI_3, $Sb(CH_3)_3$, Sb_4O_6, $SbCl_5$	„	Sb compounds with those of As and Bi	120	120	[44] Antimony bromide: reduction of antimony oxide; also analysis of antimony sulphide	40	

Tellurium . .	TeH_2, $TeCl_4$, $TeCl_2$	Directly	Most Te compounds with those of S and Se	125	125	[45] Oxidation of tellurium: potassium-tellurium bromide; synthesis of basic tellurium sulphate and of copper telluride	62·5	
Iodine . . .	IH, ICl, $I(CH_3)$, I_2P_4, I_2Hg, I_3P, I_3As, I_4Si, I_6Al_2, &c.	"	Iodides with analogous compounds of Cl and Br	126·53	126·53	[46] Silver iodate: silver iodide: synthesis of do.	126·53	
Cæsium . . .	CsCl	Indirectly: doubtful [comparison of compounds with those of other alkali metals]	Cs compounds with those of other metals of alkalis	132·7	—	[47] Cæsium chloride	132·7	
Barium . . .	None	Indirectly: doubtful [comparison of compounds of Ca, Sr, Ba]	Ba compounds with those of Ca and Sr	—	—	[48] Barium chloride	68·4	*Ba.* Atomic weight is 68·4 × 2 = 136·8, because of analogies between salts of Ba, Sr, and Ca
Lanthanum .	"	Directly	Most La compounds with those of Ce, Di, Er, and Yt. Some compounds of these metals with Ca compounds	—	138·5	[49] Lanthanum sulphate; do. oxide; do. oxalate	46·17	
Cerium . . .	"	"		—	139·9	[50] Cerium oxalate; do. chloride; do. sulphate	46·6	
Didymium .	"	"		—	144	[51] Didymium oxide and sulphate	48	
					(142)	[51a] "	(47·6)	
Erbium . . .	"	Sp. heats of a few compounds determined		—	—	[52] Erbium sulphate	55·3	*Er.* This metal belongs to the earth group, hence the atomic weight is taken as 55·33 × 3 = 166.
Ytterbium .	"	"	[? A few Yb compounds with those of other earth metals]	—	—	[53] Ytterbium sulphate	57·69	*Yb.* For similar reasons to those which apply in cases of Sc, Yt, and Er, the atomic weight of Ytterbium is supposed to be 3 times its combining weight = 173
Tantalum . .	$TaCl_5$	—	Ta with Nb compounds	182	—	[54] Potassium-tantalum fluoride; ammonium-tantalum fluoride	60·67	
Tungsten . .	$WOCl_4$, WCl_6, WCl_5	Directly	W with Mo compounds. Some salts of H_2WO_4 with those of H_2CrO_4 and H_2TeO_4	183·6	183·6	[55] Reduction of tungstic oxide; tungsten hexachloride	30·6	

[32] **Sr.** Marignac, *A.* 106, 168. Dumas, *A. Ch.* [3] 55, 191.
[33] **Yt.** Cleve, *B.* 6, 1467. Rammelsberg, *B.* 9, 1580.
[34] **Zr.** Hermann, *J. pr.* 31, 77. Marignac, *A. Ch.* [3] 60, 257.
[35] **Nb.** Marignac, *Fr.* 5, 480.
[36] **Mo.** P. Liechti a. B. Kempe, *A.* 169, 344.
[37] **Ru.** Claus, *P.* 65, 218. Joly, *C.R.* 107, 994; 108, 946.
[38] **Rh.** Berzelius, *P.* 13, 437. Seubert a. Kobbé, *A.* 260, 314.
[39] **Pd.** Berzelius, *P.* 13, 442.
[40] **Ag.** Stas, *Rapports*, 38, 42, 44; and *Nouvelles Recherches*, 109, 158, 171, 189, 193, 206
[41] **Cd.** O. W. Huntington, *P. Am. A.* 17, 28; *C. N.* 44, 268.
[42] **In.** C. Winckler, *J. pr.* 94, 8; 102, 282. Bunsen, *P.* 141, 28.
[43] **Sn.** Dumas, *A. Ch.* [3] 55, 154.
[44] **Sb.** R. Schneider, *Ueber das Atomgewicht des Antimons* (Berlin), 1880. J. P. Cooke, *P. Am. A.* 13, 1; 17, 13. J. Bongartz, *B.* 16, 1942.
[45] **Te.** W. L. Wills, *C. J. Trans.* 1879, 704. Brauner, *B.* 16, 3055.
[46] **I.** Stas, *Nouvelles Recherches*, 135, 152, 189, 193.
[47] **Cs.** Bunsen, *P. A.* 119, 1. Johnson a. Allen, *Am. S.* [2] 35, 94. R. Godeffroy, *A.* 181, 185.
[48] **Ba.** Marignac, *A.* 68, 215. Dumas, *A. Ch.* [3] 55, 137.
[49] **La.** Marignac, *A. Ch.* [4] 30, 67. Cleve, *Bl.* 50, 212; [2] 39, 151. Brauner, *C. J. Trans.* 1882, 75.
[50] **Ce.** Marignac, *A.* 68, 212. H. Buhrig, *J. pr.* [2] 12, 222. Robinson, *Pr.* 37, 150. Brauner, *C. J. Trans.* 1885, 879.
[51] **Di.** B. Brauner, *C. J. Trans.* 1882, 68.
[51a] **Di.** P. T. Cleve, *Bl.* [2] 39, 289.
[52] **Er.** P. T. Cleve, *C. R.* 91, 381. Nilson, *B.* 13, 1459.
[53] **Yb.** Nilson, *B.* 12, 550; 13, 1430.
[54] **Ta.** Marignac, *A. Suppl.* [4] 351.
[55] **W.** Roscoe, *C. N.* 25, 61, 73.

I. Element	II. Principal compounds vapour densities of which have been determined	III. Specific heat: how determined	IV. Isomorphism: compounds compared [see Note A, p. 361]	V. Atomic weight (1) By vapour density method	V. Atomic weight (2) By sp. heat method	VI. Compounds analysed, &c. in order to find combining weight of the element [see note B, p. 361]	VII. Combining weight [Note B, p. 361]	VIII. Remarks [See Note C, p. 361]
Osmium	OsO_4	Directly	Os, Ir, and Pt compounds with those of Ru, Rh, and Pd	190·3	190·3	[56] Osmium tetroxide	47·57	
Iridium	None	"		—	192·5	[57] Potassium - iridium chloride	48·125	
Platinum	"	"		—	194·3	[58] Potassium - platinum chloride, platinum tetrachloride and bromide, &c.	48·575	
Gold	"	"	Some Au compounds with those of Ag. A few Au compounds with those of Ni and Fe	—	197	[59] Gold chloride; potassium-gold chloride and bromide	65·66	
Mercury	$[HgCl]$, $HgCl_2$, HgI_2, $Hg(CH_3)_2$, &c.	"	Hg and Cu compounds of type RO	199·8	199·8	[60] Mercuric chloride; do. oxide	99·9	
Thallium	$TlCl$	"	Tl compounds with those of type RCl_3. Tl compounds of type TlCl with those of alkali metals	203·64	203·64	[61] Synthesis of thallium nitrate	203·64	
Lead	$PbCl_2$, $Pb(CH_3)_4$	"	Some Pb with Tl compounds; many Pb with Cu and Hg compounds	206·4	206·4	[62] Synthesis of lead nitrate; do. sulphate	103·2	
Bismuth	$BiCl_3$, BiF_3, $Bi(CH_3)_3$, &c.	"	Bi compounds with those of As and Sb	208	208	[63] Synthesis of bismuthous oxide; bismuthous chloride	69·33	
Thorium	$ThCl_4$	"	ThO_2 with SiO_2, TiO_2, SnO_2, and ZrO_2	231·87	231·87	[64] Thorium sulphate	57·97	
Uranium	UCl_4, UBr_4	"	Some U compounds of type U_2O_3 with those of Al, Cr, Mn, and Fe	240	240	[65] Uranium acetate; do. oxalate	60	

[56] **Os.** Deville a. Debray, *A. Ch.* [3] 56, 403
[57] **Ir.** K. Seubert, *B.* 11. 1767.
[58] **Pt.** K. Seubert, *B.* 14, 865; *A.* 207, 29. W. Halberstadt, *B.* 17, 2962.
[59] **Au.** Berzelius, *Lehrbuch* (5th ed.), 3, 1212. Javal, *A. Ch.* 17, 337. Levol, *A. Ch.* [3] 30, 355. Thorpe a. Laurie, *C. J.* 51. 565. Krüss, *B.* 20. 205.
[60] **Hg.** Erdmann a. Marchand, *J. pr.* 31, 392. Svanberg, *J. pr.* 45, 468. Millon, *A. Ch.* [3] 18, 345.
[61] **Tl.** W. Crookes, *T.* 1873. 277.
[62] **Pb.** Stas, *Rapports*, 101, 106.
[63] **Bi.** Schneider, *P.* 82, 303. Dumas, *A. Ch.* [3] 55, 176; Marignac, *Ar. Ph.* [3] 10, 5, 193. Löwe, *Fr.* 22, 498. Schneider, *J. pr.* [2] 30, 237.
[64] **Th.** Nilson, *B.* 15, 2527. Krüss a. Nilson, *B.* 20, 1665.
[65] **U.** Peligot, *A. Ch.* [3] 20, 329.

Notes to Table of Atomic Weights.

A. **As the method based on isomorphism of compounds is chiefly used as a means of verifying values assigned to atomic weights by other methods, no numbers are given in column IV., but merely an indication of the various compounds which have been compared crystallographically, and on which arguments for or against a given value for the atomic weights in column V. have been, or may be, based.**

B. This column (VI.) is not to be regarded as containing anything like a complete summary of the processes employed for determining the combining weights of the elements; only the more important processes are indicated—references are given to the original papers.

By *combining weight* is here meant the smallest mass of the element which combines with 8 parts by weight of oxygen, 1 part of hydrogen, or 35·5 parts of chlorine.

A complete account of all researches on this subject will be found in *A Recalculation of the Atomic Weights*, by F. W. Clarke [Part v. of the *Constants of Nature* published by the Smithsonian Institution], and also in *Die Atomgewichte der Elemente*, by L. Meyer and K. Seubert [Leipzig, 1883].

C. When the atomic weight given in column V. section (2) is a multiple of the combining weight in column VII., no number being given in section (1) of column V., it is to be inferred that, besides the argument drawn from the value of the specific heat of the element in question, there are other chemical reasons for adopting the special multiple which appears in V. (2); these reasons may be broadly described as based on analogies between salts of the given element and salts of other elements the atomic weights of which have been established by the two leading physical methods. M. M. P. M.

ATOMICITY. Term used to denote number of atoms in any specified gaseous molecule, usually in the molecule of an element.

ATOMIC VOLUMES *v.* PHYSICAL METHODS; sect. VOLUMETRICAL.

ATRACTYLIC ACID $C_{30}H_{51}S_2O_{18}$. Potassium atractylate K_3A''' occurs in the root of *Atractylis gummifera*, from which it may be extracted by boiling 70 p.c. alcohol (Lefranc, *Bl.* [2] 11, 499; *J. Ph.* [4] 9, 81; 10, 325; 17, 187, 263; *C. R.* 67, 954; 76, 438). Boiling potash hydrolyses it, forming valeric acid and so-called (β)-atractylic acid, $C_{20}H_{38}S_2O_{16}$, which is further split up into H_2SO_4, valeric acid and atractylin.

ATRACTYLIN $C_{20}H_{30}O_6$. From '(β)-atractylic acid' by boiling with aqueous KOH. White gummy substance, with sweet taste, v. sol. water and alcohol, insol. ether and aqueous NaCl. Forms a violet-red solution in warm H_2SO_4. Boiling KOH forms atractyligenin and a saccharine substance.

ATRANORIC ACID $C_{19}H_{18}O_8$. [190°-194°]. Extracted by ether from certain lichens (*Lecanora atra, Stereocaulon vesuvianium, Cladonia rangiformis*). Trimetric crystals; $a:b:c = 1:·398:·306$; sl. sol. alcohol, cold ether, and benzene; m. sol. hot benzene; sol. alkalis forming a yellow solution. Heated with water in a sealed tube it splits up into atranorinic acid, $C_9H_{10}O_4$, and atraric acid, $C_{10}H_{10}O_5$ (Paternò, *G.* 9, 279; 10, 157; 12, 256; Coppola, *G.* 12, 19).

ATRANORINIC ACID $C_9H_{10}O_4$. [101°]. Formed by heating atranoric acid (*q.v.*) with water. Needles, m. sol. water, sol. alcohol and ether. Its alkaline solutions are yellow. Its aqueous solutions give a green pp. with $AgNO_3$, a brownish-green colour with Fe_2Cl_6, and a blood-red colour with bleaching-powder (Paternò, *G.* 12, 256).

ATRARIC ACID $C_{10}H_{10}O_5$. [141°]. Produced by heating atranoric acid with water (Paternò, *G.* 12, 257). Iridescent laminæ, sl. sol. water, m. sol. alcohol and ether. Its alkaline solutions are colourless. It gives a brownish pp. with $AgNO_3$ and no colour with Fe_2Cl_6.

ATRIPAÏC ACID $C_6H_8O_{12}$6aq. [98° when hydrated]. An acid obtained from the sugar cane (Savary, *C. C.* 1884, 968).

Ethyl ether (184°-188°).

ATROGLYCERIC ACID $C_9H_{10}O_4$ *i.e.* $CH_2(OH).CPh(OH).CO_2H$. [146°]. *αβ-Di-oxy-α-phenyl-propionic acid.* From αβ-di-bromo-α-phenyl-propionic acid and excess of alkali (Kast, *A.* 206, 30). Crystalline aggregates, sol. water and ether. Salts.—CaA'_2.—BaA'_2.

Nitrile $CH_2OH.CPh(OH).CN$. [57°]. From benzoyl-carbinol and HCN (Plöchl a. Blümlein, *B.* 16, 1292).

ATROLACTIC ACID *v.* α-OXY-α-PHENYL-PROPIONIC ACID.

ATROLACTYL-TROPEÏNE $C_8H_{14}NOC_9H_9O_2$. *Pseudo-atropine.* [121°]. Crystalline solid. Very similar in physiological action to atropine. Formed by the action of dilute HCl on tropine atrolactate.

Salts.—Mostly soluble.—$B'HClAuCl_3$: sparingly soluble tables. The picrate also forms sparingly soluble tables (Ladenburg a. Roth, *B.* 15, 1027; *A.* 217, 87).

ATRONENE $C_{16}H_{14}$ *i.e.* $C_6H_4\left\langle\begin{matrix} CH_2-CH \\ \| \\ CPhH.CH \end{matrix}\right.$.

Phenyl-naphthalene dihydride. (325° i.V.) Formed, together with atronic acid, by the dry distillation of (α)- or (β)-iso-atropic acid (Fittig, *A.* 206, 51). Liquid. *Chromic acid* oxidises it to *o*-benzoyl-benzoic acid.

Atronene sulphonic acid $C_{16}H_{13}SO_3H$. [130°]. Needles; v. sol. water.—BaA'_2.—$CaA'_2$2aq.

ATRONIC ACID $C_{17}H_{14}O_2$ *i.e.* $C_6H_4\left\langle\begin{matrix} CH(CO_2H) \\ CPhH.CH \end{matrix}\right\rangle CH$. (?) *Phenyl-naphthalene di-hydride carboxylic acid* (?). [164°]. Formed, together with atronene by the dry distillation of (α)- or (β)-iso-atropic acid (Fittig, *A.* 206, 46). Prisms; insol. water, sol. alcohol and glacial HOAc. Salts.—$CaA'_2$6aq.—$BaA'_2$4aq.

Iso-atronic acid $C_{17}H_{14}O_2$. [157°]. Obtained by heating (α)-, or (β)-, iso-atropic acid with conc. H_2SO_4 (Fittig, *A.* 206, 86). Leaflets, insol. water, sol. alcohol, ether, and glacial HOAc.

Salts.—CaA'_2.—$BaA'_2$6aq.

ATRONYLENE SULPHONIC ACID $C_{16}H_{11}.SO_3H$. [c. 258°]. Formed by heating (α)-, or (β)-, iso-atropic acid or iso-atronic acid with 9 pts. conc. H_2SO_4 at 90° (Fittig, *A.* 206, 60). Prisms (from 50 p.c. acetic acid). Insol. water, v. sol. alcohol. The aqueous solutions of its salts when exposed to sunlight deposit small

needles of **atronyl-sulphone** $C_{18}H_{16}SO_2$. [193°].

ATROPIC ACID $C_9H_8O_2$ *i.e.* CH_2:CPh.CO_2H. *a-Phenyl-acrylic acid.* M. w. 148. [107°]. (203°) at 75 mm. S. ·141 at 19°.

Formation.—1. By boiling atropine with baryta (Richter, *J. pr.* 11, 33; Kraut, *A.* 128, 282; Fittig a. Wurster, *A.* 195, 147).—2. By heating atropine with fuming HCl at 120° (Lossen, *A.* 138, 230). 3. By the action of HCl on ethyl-tropic acid, CH_3.CPh(OEt).CO_2H, obtained from acetophenone chloride by alcoholic KCN and saponification (Ladenburg a. Rügheimer, *B.* 13, 2041).—4. By action of boiling NaOH upon a-chloro-β-phenyl-propionic acid which is formed by the action of HCl upon acetophenone cyanhydrin or by heating a-oxy-a-phenyl-propionic acid with saturated HClAq at 130° (Spiegel, *B.* 14, 237; 1354).

Properties.—Needles (from water) or monoclinic prisms (from alcohol); v. sol. CS_2.

Reactions.—1. *Chromic acid mixture* forms benzoic acid.—2. *Potash-fusion* forms phenyl-acetic acid.—3. *Sodium-amalgam* reduces it to a-phenyl-propionic acid.—4. Fuming HCl forms a-chloro-a-phenyl-propionic acid, which is converted by aqueous Na_2CO_3 at 120° into tropic acid, CH_2(OH).CPhH.CO_2H.—5. ClOH forms chloro-tropic acid CH_2(OH).CPhCl.CO_2H (Ladenburg a. Rügheimer, *B.* 13, 376).—6. Cold conc. HBrAq forms both a-, and β-, bromo-a-phenyl-propionic acid; at 100° it forms only β-bromo-a-phenyl-propionic acid.—7. *Bromine* forms CH_2Br.CPhBr.CO_2H.

Salts.—Neutral atropates are not ppd. by manganous salts (difference from cinnamates).—CaA'_2 5aq (K.).—CaA'_2 2aq (L.).

(a)-**Iso-atropic acid** $C_{18}H_{16}O_4$ (?). [237°].

Preparation.—(a)-, and (β)-, isoatropic acids are both formed when atropic acid is heated alone or with water; they may be separated by crystallisation from 50 p.c. acetic acid.

Properties.—Crystalline aggregates, sl. sol. boiling water, sol. alcohol. *Chromic acid* gives anthraquinone and *o*-benzoyl-benzoic acid. *V.* also ATRONENE, ATRONIC ACID, and ATRONYLENE SULPHONIC ACID.

Salts.—CaA″2aq.—BaA″$2\frac{1}{2}$aq.

Ethyl ether Et_2A'' (180°).

(β)-**Iso-atropic acid** $C_{18}H_{16}O_4$. [206°]. Rectangular tables (from water). More soluble in water, alcohol, and HOAc than the (a) acid. Gives the same reactions as the (a) acid.

Salts.—CaA″3aq (Fittig, *A.* 206, 34; *B.* 12, 1739; compare R. Meyer, *A.* 219, 290).

ATROPINE $C_{17}H_{23}NO_3$ *i.e.*
CH_2OH.CPhH.CO.O.CH_2.CH_2.C_5H_7NMe.
Daturine. [114°]. S. ·33.

Occurrence.—Together with hyoscyamine in all parts of *Atropa belladonna* (Geiger a. Hesse, *A.* 5, 43; 6, 44; Mein, *A.* 6, 67), and in the seeds of *Datura stramonium* (Geyger, *A.* 7, 272; Planta, *A.* 74, 245).

Formation.—Crystalline tropine tropate has no action on the eyes, but when treated with dehydrating agents, such as $ZnCl_2$, Ac_2O, or HCl, atropine is formed. It is best to evaporate frequently with very dilute HCl at 100° (Ladenburg, *A.* 217, 78; *B.* 12, 942; 13, 104, 909; *C. R.* 90, 921). Tropine contains hydroxyl which is etherified by tropic acid:

CH_2(OH).CPhH.CO_2H + HO.CH_2.CH_2.C_5H_7NMe = CH_2(OH).CPhH.CO.O.CH_2.CH_2.C_5H_7NMe + H_2O

Preparation.—Dry belladonna leaves are digested for three days with cold water, the extract is evaporated, and after mixing with Na_2CO_3 the syrupy liquid is agitated with benzene. The benzene solution is decanted off and shaken with dilute sulphuric acid. The acid liquid is rendered alkaline with Na_2CO_3 and the solution agitated with chloroform; the extract is filtered and, after addition of light petroleum, allowed to evaporate spontaneously, when the atropine separates out first, the mother liquors containing another alkaloid (Pesci, *G.* 10, 426).

Properties.—Needles (from dilute alcohol). Sl. sol. water; v. sol. alcohol, and chloroform, m. sol. ether. The solutions are alkaline to test-paper, and taste bitter. Its salts enlarge the pupil of the eye. ·05 to ·2 g. is a fatal dose. Three drops of a 1 p.c. solution of (artificial) atropine enlarges the pupil to the maximum extent. Atropine overcomes the stoppage of the heart's action produced by muscarine.

Reactions.—1. When evaporated to dryness with fuming HNO_3 a residue is left which is turned violet by alcoholic KOH.—2. *Chromic acid mixture* forms benzoic acid.—3. A solution in HCl gives with *gold chloride* an oily pp. that quickly changes to lustreless crystals which melt under water or, when dry, at 136°.—4. *Tannin* gives, in very dilute neutral solutions a white pp., sol. HCl.—5. *Potassio-mercuric iodide* gives a white cheesy pp.—6. I in KI gives a brown oil which solidifies after some time.—7. *Picric acid* gives, in somewhat dilute acid solutions, a crystalline pp.—8. Conc. H_2SO_4 gives, on warming, a pleasant odour.—9. *Cyanogen* gas passed into an alcoholic solution gives, after some time, a red colour.—10. *Chloride of iodine* forms a dark yellow pp., sol. on warming, and separating out on cooling in brown crystals (Dittmar, *B.* 18, 1612).—11. Decomposed by hot *baryta-water* or cold conc. HCl into tropic acid and tropine (Kraut, *A.* 128, 280; 133, 87; 148, 240; Lossen, *A.* 138, 230).—12. Hot conc. HClAq at 120° gives tropine, tropic acid, atropic acid, iso-atropic acids, and (at 180°) tropidine.—13. With $NaNO_2$, H_2SO_4, and subsequently NaOH a violet colour is developed.—14. Glacial HOAc and H_2SO_4 produce on prolonged warming a greenish-yellow fluorescence (Flückiger, *Ph.* [3] 16, 800).—15. H_2SO_4 and $KClO_3$ give a greenish-blue colour (Vitali, *Ph.* [3] 12, 459).

Salts.—B'HAuCl$_4$ [135°–137°].—B'$_2$H$_2$PtCl$_6$ [208°].—B'HCl 2HgCl$_2$ (Gerrard, *Fr.* 24, 601). B'HI$_2$: brown prisms (Jörgensen, *Z.* 5, 673).—B'HI$_4$.—B'$_2$H$_2$SO$_4$: needles, got by adding an ethereal solution to an alcoholic solution of H_2SO_4. Valerate B'$C_5H_{10}O_2$ $\frac{1}{2}$aq [42°] (Callmann, *J. pr.* 76, 69).

Additional References.—Günther, *J.* 1869, 781; *Fr.* 8, 476; Lefort, *Ph.* [3] 2, 1029; *C. C.* 1873, 797; Brunner, *B.* 6, 96; Newark, *C. C.* 1872, 536; Guliolmo, *Fr.* 2, 404; Ludwig, *Ar. Ph.* [2] 107, 129; Schmidt, *A.* 208, 196.

Ethyl-atropine $C_{17}H_{22}EtNO_3$. Formed by action of Ag_2O on its hydriodide, B'HI, obtained

by heating atropine with EtI at 100° (Lossen, *A.* 138, 239). A syrup, sol. water.

Apoatropine $C_{17}H_{21}NO_2$. [60°-62°]. Formed by treating atropine with HNO_3 (Pesci, *G.* 11, 538; 12, 60). Prisms; sl. sol. water, v. e. sol. alcohol. Decomposed by baryta-water at 100° into tropine and atropic acid. Does not enlarge the pupil. Salts.—$B'HAuCl_4$ [180°] amorphous.—$B'H_2SO_4$ 5aq.

Pseudo-atropine *v.* ATROLACTYL-TROPEÏNE.

Hydro-apo-atropine
$CH_3.CHPh.CO.O.CH_2.CH_2.C_5H_7NMe$. Prepared by the action of nascent hydrogen on apoatropine (Pesci, *Atta d. Acad. dei Lincei*, 5, 329). Oil. Decomposed by baryta-water at 100° into α-phenyl-propionic acid and tropine. Forms a crystalline compound with $HgCl_2$. Neutral $KMnO_4$ oxidises it to 'homo-apo-atropine' $C_{16}H_{21}NO_2$, an alkaline oil which forms the following salts: B'_2CO_3, $B'_2H_2PtCl_6$, $B'HAuCl_4$, $B'_2H_2SO_4$ *x*aq, $B'_2H_2PdCl_6$; its hydrochloride gives white pps. with tannin, Mayer's reagent, and $HgCl_2$; and it gives a blood-red colour with fuming HNO_3; heated with baryta-water it gives α-phenyl-propionic acid and tropigenine (Pesci, *G.* 12, 285, 329; Merling, *B.* 15, 289).

Homo-atropine *v.* PHENYLGLYCOLYL-TROPEÏNE.

Meta-atropine *v.* TROPINE.

ATROPYL-TROPEÏNE $C_{17}H_{21}NO_2$. *Anhydro-atropine.* Obtained by heating tropine hydrochloride with atropic acid and HCl (Ladenburg, *A.* 217, 102; *B.* 13, 1085). Oil.—$B'HAuCl_4$: small needles.

ATROXINDOLE *v.* o-AMIDO-α-PHENYL-PROPIONIC ACID, p. 179.

AURANTIIN $C_{23}H_{26}O_{12}$ 4aq. [171°]. S. ·33. $[\alpha]_j = -64{\cdot}57°$. A glucoside in the flowers of *Citrus decumana* (E. Hoffmann, *B.* 9, 691). Yellow monoclinic prisms. Bitter taste. Gives a brownish-red colour with Fe_2Cl_6.

AURATES. Auric hydroxide $Au_2O_4H_2$ ($=Au_2O_3.H_2O$) reacts with HNO_3Aq to form the compound $Au(NO_3)_3.HNO_3.3H_2O$; from this several basic nitrates and one or two sulphates of gold may be produced (Schottländer, *A.* 217, 312). But $Au_2O_3.H_2O$ also dissolves in KOHAq, and on evaporation at a gentle heat and finally *in vacuo*, crystals are obtained, which when dissolved in water, recrystallised, drained, and dried *in vacuo*, are said to have the composition $Au_2O_3.K_2O.3H_2O$ ($=Au_2O_4K_2.3H_2O$). Aurate of potassium is very soluble in water, forming an alkaline liquid which is easily decomposed by organic compounds and by heat; the solution gives pps. with solutions of various metallic salts, *e.g.* $CuCl_2$; these pps. are said to be aurates, but very little is known about their composition. An aurate of ammonium of indefinite composition, known as *fulminating gold*, is formed by pptg. a solution of a gold salt by excess of NH_3Aq, and boiling in NH_3Aq; or by digesting $Au_2O_3H_2O$ in $(NH_4)_2SO_4Aq$ (Fremy, *A. Ch.* [3], 31, 480; Figuier, *id.* [3] 11, 341). M. M. P. M.

AURIC ACID. The hydrated oxide of gold $Au_2O_3H_2O$ is sometimes called auric acid because of its salt-forming reactions with alkalis (*v. supra*). This compound is best prepared by adding NaOHAq to very dilute $AuCl_3Aq$, in the ratio $8NaOH:AuCl_3$, (the $AuCl_3Aq$ should be prepared in about the ratio $AuCl_3:800H_2O$); warming till the liquid is dark brown; adding Na_2SO_4Aq; allowing pp. to settle; washing repeatedly by decantation, and then on a filter, until the washings are free from H_2SO_4 and HCl; boiling pp. with conc. HNO_3Aq; and again washing free from acid (Thomsen, *Th.* 3, 391). According to Krüss (*B.* 19, 2546), $Au_2O_3.H_2O$ is better prepared from Au_2Cl_6Aq by ppg. with *magnesia alba*, boiling with dilute HNO_3Aq, washing with water, and drying over P_2O_5. $Au_2O_3.H_2O$ is easily soluble in HBrAq and HClAq, with production of much heat, and formation of $AuCl_4HAq$ and $AuBr_4HAq$ respectively (*v.* GOLD). M. M. P. M.

AURINE *v.* ROSOLIC ACID.

AUSTRALENE *v.* TURPENTINE OIL.

AXIN *v.* AGE, p. 87.

AZAMMONIUM COMPOUNDS. Compounds obtained by oxidising mono-alkylated o-amido-azo compounds, or by heating azimido-compounds with alkyl iodides followed by moist Ag_2O (Zincke a. Lawson, *B.* 20, 1173). Thus $C_6H_5.N:N.C_{10}H_6.NH.C_6H_5$ gives, on oxidation with chromic acid, $C_{22}H_{17}N_3O$ which might be expected to have the formula:

$$C_{10}H_6\left\langle\begin{array}{l}N(OH).C_6H_5\\ \ |\quad\diagdown\\ N—N.C_6H_5\end{array}\right. .$$

Naphthalene - di - phenyl - azammonium hydrate

$$C_{22}H_{16}N_3.OH \ \textit{i.e.}\ C_{10}H_6\left\langle\begin{array}{l}N(OH).C_6H_5\\ \ |\quad\diagdown\\ N.N.C_6H_5\end{array}\right. \quad (?).$$

The chromate is obtained by the oxidation of benzene-azo-phenyl-(β)-naphthylamine

$$C_{10}H_6\left\langle\begin{array}{l}N.C_6H_5\\ \ |\\ N.NHC_6H_5\end{array}\right. \quad (?)$$ with $K_2Cr_2O_7$ and acetic acid. It is converted into the chloride by boiling with alcohol and HCl till all the chromic acid is reduced. The hydrate is obtained from the chloride by Ag_2O. Its solution has a greenish fluorescence, is strongly alkaline, and tastes bitter; it decomposes on evaporation.

Salts.—Like the base, they have a greenish fluorescence in aqueous and alcoholic solution, and a bitter taste. — $C_{22}H_{16}N_3Cl$: glistening prisms, v. sol. alcohol, less in water; it forms sparingly soluble double chlorides with $SnCl_2$, $ZnCl_2$, $HgCl_2$, &c.—$(C_{22}H_{16}N_3Cl)_2PtCl_4$: sl. sol. crystalline pp. — $C_{22}H_{16}N_3.HSO_4$: glistening transparent needles or prisms, v. sol. hot alcohol, sl. sol. cold water. — $C_{22}H_{16}N_3NO_3$: long flat glistening needles, v. sol. hot alcohol, sl. sol. water. — $(C_{22}H_{16}N_3)_2Cr_2O_7$: long yellow needles, sol. acetic acid, v. sl. sol. water.—*$(C_{22}H_{16}N_3)C_6H_2(NO_2)_3O$: [243°]; small yellow needles, v. sl. sol. water (Zincke a. Lawson, *B.* 20, 1172).

AZARONE $C_{12}H_{16}O_3$. [59°]. (296°). S.G. $\frac{18}{18}$ 1·165; $\frac{60}{60}$ 1·0743. Obtained by distilling the rhizomes of *Azarum europæum* with steam (Boutléroff a. Rizza, *Bl.* [2] 43, 114). White crystalline body, sl. sol. water, sol. alcohol, ether CCl_4, and acetic acid. Combines with Br, forming $C_{12}H_{16}Br_2O_3$.

AZAUROLIC ACIDS.

Ethyl-azaurolic acid $C_4H_4N_2O$. [142°]. From ethyl nitrolic acid (2 g.) by the action of water and sodium amalgam. The yield (·25 g) is bad. Formed also by reducing di-nitro-ethane (V. Meyer a. Constam, *A.* 214, 330; *B.* 14, 1455).

Properties.—Orange-red prisms (from alco-

hol). M. sol. hot alcohol, sl. sol. ether, v. sl. sol. water, chloroform, benzene or light petroleum. Alkalis form a deep orange solution. At 142° it melts, with decomposition, leaving a liquid which, after solidifying, melts again at 133°.

Reactions.—1. Ammoniacal solution gives with $AgNO_3$ a brown pp., and with salts of Zn or Pb, yellow pps. A solution of the ammonium salt deposits, on evaporation, needles of the free acid. 2. *Heat, dilute acids, nascent hydrogen,* and *ammonia* all convert it into ethyl-leucazone: $2C_2H_4N_2O + H_2O = C_4H_7N_3O + O + NH_3O$ the oxygen converting another portion of ethyl-azaurolic acid into acetic acid, N, and N_2O.—3. $K_2Cr_2O_7$ and H_2SO_4 give acetic acid and CO_2.

Constitution.—Its formation from ethyl-nitrolic acid indicates the group $\mathrm{MeC}\!<\!\begin{matrix}\mathrm{N}\\\mathrm{N}\end{matrix}$, and the presence of Me.C is shown by the production of acetic acid on oxidation. Ethyl-azaurolic acid would then be $\mathrm{Me.CH}\!<\!\begin{matrix}\mathrm{N}\\\mathrm{N}\end{matrix}\!>\!\mathrm{O}$ or, more probably, MeCH(NO).N:N.CH(NO)Me or perhaps MeC(NO):N.NH.CMe:NOH.

Ethyl-leucazone $C_4H_7N_3O$. [158°]. Formed together with nitrogen, N_2O, and hydroxylamine by heating ethyl-azaurolic acid with dilute HCl (M. a. C.). Satiny needles. Reddens litmus. Combines with acids, bases, and salts. V. sol. alcohol or water, insol. ether. Its aqueous solution is turned red by Fe_2Cl_6 and oxidised to acetic acid by $K_2Cr_2O_7$ and H_2SO_4.

Salts.—$B'_2H_2SO_4$: [161·5°]; prisms, sol. ordinary (90 per cent.) alcohol.—$Ba(C_4H_6N_3O)_2$.—$C_4H_7N_3OAgNO_3$.

Propyl-azaurolic acid $C_3H_6N_2O$. [127·5°]. From propyl-nitrolic acid by sodium-amalgam.

AZELAIC ACIDS $C_9H_{16}O_4$.

***n*-Azelaïc acid**

$CO_2H.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CO_2H$. [118°]. Formed by reducing butyro-furonic acid with HI and P (Tönnies, *B.* 12, 1200). Slender needles (from chloroform).

Azelaïc acid $C_9H_{16}O_4$. *Anchoic acid. Lepargylic acid.* Mol. w. 188. [106°]. (above 360°). S. ·108 at 12°; S. (ether) 1·88 at 11°.

Formation.—1. By the oxidising action of HNO_3 upon Chinese wax (Buckton, *C. J.* 10, 166), cork, oleïc acid (Laurent, *A. Ch.* [2] 66, 154), cocoa-nut oil (Wirz, *A.* 104, 265), castor oil (Arppe, *A.* 120, 288; Ganttner a. Hell, *B.* 14, 560, 1545), and œnanthoic acid (Krafft, *B.* 11, 1415).—2. From oleïc and $KMnO_4Aq$ (Saytzeff, *J. pr.* [2] 33, 301).

Preparation.—Castor oil is oxidised by HNO_3 (S.G. 1·25). Heptoic acid is distilled off with steam, and the hot residual liquor poured off from a heavy nitrogenous oil. On cooling, suberic and azelaïc acids crystallise. Pure suberic acid is got by washing the mixed acids with ether, which dissolves azelaïc acid as well as oily impurities. The ether is evaporated, the residue dissolved in boiling water and NaCl added. Oily matter then separates and azelaïc acid crystallises from the brine (Dale a. Schorlemmer, *C. J.* 35, 684; *cf.* Ganttner a. Hell, *B.* 14, 1545).

Properties.—Large thin plates, not volatile with steam. Sol. water, alcohol, and ether. *Nitric acid* oxidises it to succinic acid. It does not give a homologue of suberone when distilled with slaked lime, hence its constitution is probably not analogous to that of the homologous suberic acid.

Salts.—K_2A'': small plates.—$K_2A''2aq$: needles.—KHA''.—$KH_3A''_2$.—$Na_2A''aq$: soluble plates.—$Na_3HA''_2$.—$(NH_4)_2A''$: large plates.—$(NH_4)HA''$.—$BaA''aq$: S. ·65 at 16°; ·628 at 100°.—$SrA''aq$.—CaA'': crystalline powder; S. ·185 at 17°; ·193 at 100°.—$MgA''3aq$.—$MnA''3aq$: slender needles; S. ·206 at 14°; ·108 at 100°.—$NiA''6aq$.—$CoA''6aq$.—ZnA'': crystalline pp.; S. ·026 at 12°.—PbA'': white pp.; S. ·006 at 24°.—Ag_2A'': white pp.; S. ·0015 at 14°.—CuA''.—$Fe(OH)A''2aq$.—CdA''.

Ethyl ether Et_2A''. (260°). Decomposed on boiling.

AZIDINES. Compounds related to hydrazines (*q. v.*) in the same way that amidines are related to amines. Thus the hydrochloride of phenyl-hydrazine acting on a solution of benzimido-ether in absolute alcohol produces dark red needles of di-phenyl-benz-azidine, Ph.C(NH.NPhH):N.NPhH; while form-imido-ether gives, when similarly treated, di-phenyl-formazidine CH(NH.NPhH):N.NPhH [185°] (Pinner, *B.* 17, 182, 2002).

AZIMIDO- COMPOUNDS. This term was originally applied by Griess (*B.* 15, 1878) to the compounds obtained by the action of nitrous acid upon ortho-diamines, which are probably of the form $\mathrm{R''}\!<\!\begin{matrix}\mathrm{N}\\|\\\mathrm{N}\end{matrix}\!>\!\mathrm{NH}$, and was extended by Zincke (*B.* 18, 3134) to compounds, probably of the form $\mathrm{R''}\!<\!\begin{matrix}\mathrm{N}\\|\\\mathrm{N}\end{matrix}\!>\!\mathrm{NR'}$, got by oxidising *o*-amido-azo-compounds (hydrazimido-compounds). The first formula may also be written $\mathrm{R''}\!<\!\begin{matrix}\mathrm{NH}\\\mathrm{N}\end{matrix}\!\gg\!\mathrm{N}$, which stands to $\mathrm{R''}\!<\!\begin{matrix}\mathrm{NH_2}\\\mathrm{N_2Cl}\end{matrix}$ in the relation that diazobenzene anilide stands to a mixture of diazobenzene chloride and aniline.

Azimido-benzene $C_6H_5N_3$ *i.e.* $\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{N}\\|\\\mathrm{N}\end{matrix}\!>\!\mathrm{NH}$ or $\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{NH}\\\mathrm{N}\end{matrix}\!\gg\!\mathrm{N}$. [99°]. From aqueous *o*-phenylene-diamine sulphate and KNO_2 (Ladenburg, *B.* 9, 222). Needles (from benzene).

Azimido-nitro-benzene $C_6H_4N_4O_2$ *i.e.*

$\mathrm{C_6H_3(NO_2)}\!<\!\begin{matrix}\mathrm{N}\\|\\\mathrm{N}\end{matrix}\!>\!\mathrm{NH}$ or $\mathrm{C_6H_3(NO_2)}\!<\!\begin{matrix}\mathrm{NH}\\|\\\mathrm{N_2}\end{matrix}$ [211°].

Formed by passing nitrous acid into a solution of nitro-*o*-phenylene diamine (Hofmann, *Pr.* 10, 406). Long white prisms, v. sol. alcohol and ether, sl. sol. cold water. Nitrous acid does not affect it, hence it does not contain NH_2.

Salts.—$C_6H_3KN_4O_2$.—$C_6H_3AgN_4O_2$. Not affected by boiling HCl, or KOH.

Azimido-toluene $C_7H_7N_3$ *i.e.*

$\mathrm{CH_3.C_6H_3}\!<\!\begin{matrix}\mathrm{N}\\|\\\mathrm{N}\end{matrix}\!>\!\mathrm{NH}$ or $\mathrm{CH_3.C_6H_3}\!<\!\begin{matrix}\mathrm{NH}\\\mathrm{N}\end{matrix}\!\gg\!\mathrm{N}$.

[83°]. (323°). From aqueous tolylene-*o*-diamine sulphate and KNO_2 (L.). Prisms containing C_7H_8 (from toluene). V. sol. alcohol, m. sol. ether and boiling water. Not affected by HClAq

at 160°. **Salts.**—B'HCl: decomposed by water.—$B'_2H_2PtCl_6$.

Acetyl derivative $C_7H_6AcN_3$. [130°]. From acetyl-*o*-tolylene diamine, HCl, and $NaNO_2$ (Boessneck, *B.* 19, 1758). Needles.

(β)-Azimido-benzoic acid - $C_7H_5N_3O_2$ *i.e.*

$$CO_2H.C_6H_3\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle NH \text{ or } CO_2H.C_6H_3\left\langle\begin{matrix}NH\\|\\N_2\end{matrix}\right. .$$

From the hydrochloride of di-amido-benzoic acid, $CO_2H.C_6H_3(NH_2)_2$ [1:3:4] and KNO_2 (Griess, *B.* 2, 436). Also by the action of boiling potash upon $C_6H_3(CO_2H)(NO_2)(NH.CO.NH_2)$ [1:3:4] and upon $C_6H_3(CO_2H)(NO_2)(NH.CO.NH_2)$ [1:4:3] (Griess, *B.* 15, 1880). This seems to indicate the symmetrical formula. Short needles, containing water of crystallisation; v. sl. sol. water. Not attacked by warm fuming HNO_3.

(γ)-Azimido-benzoic acid. Prepared similarly from $CO_2H.C_6H_3(NH_2)_2$ [1:2:3]. Long hair-like needles (G.).

Azimido-benzene-ν-carboxylic ether $C_9H_9N_3O_2$ *i.e.* $C_6H_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle N.CO_2Et$ or $C_6H_4\left\langle\begin{matrix}N.CO_2Et\\|\\N_2\end{matrix}\right.$. [73°]. From the hydrochloride of *o*-amido-phenyl carbamic ether and KNO_2 (Rudolph, *B.* 12, 1295).

Phenyl-azimido-naphthalene

$C_{10}H_6\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle N.C_6H_5$. [108°]. Fine white needles. Soluble in hot acetic acid, sparingly in alcohol and benzene. Formed by oxidation of benzene-azo-(β)-naphthylamine with CrO_3 in acetic acid solution. It is not attacked by strong H_2SO_4, acetic anhydride, or reducing agents (Zincke, *B.* 18, 3136).

***o*-Oxy-phenyl-azimido-naphthalene**

$C_{10}H_6\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle N.C_6H_4(OH)$ [1:2] [140°]. White silky needles. Easily soluble in alcohol and benzene. Formed by oxidation of an alkaline solution of *o*-oxy-benzene-azo-(β)-naphthylamine with lead peroxide. It is not attacked by strong H_2SO_4, acetic anhydride, acetyl chloride, or reducing agents (Z.).

***p*-Oxy-phenyl-azimido-naphthalene**

$C_{10}H_6\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle N.\overset{(1)}{C_6}H_4\overset{(4)}{(OH)}$. [199°]. Thick crystals or white needles. Soluble in hot alcohol and hot acetic acid, sparingly in benzene. Formed by oxidation of an alkaline solution of *p*-oxy-benzene-azo-(β)-naphthylamine with lead peroxide. It is not attacked by reducing agents.

Acetyl derivative

$C_{10}H_6\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle N.C_6H_4(OAc)$ [165°]; thin silky plates (Z.).

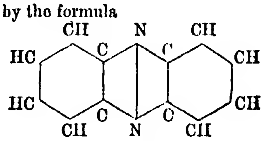
Tolyl - azimido - toluene $C_{14}H_{13}N_3$ *i.e.*

$C_7H_6\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle NC_7H_7$. [125°]. V.D. = 7·23 (for 8·32).

Formation.—1. By oxidation of *p*-toluene-*o*-azo-*p*-toluidine [1:4] $C_6H_4Me.N_2.C_6H_3Me(NH_2)$ [4:1:2].—2. By heating the imide of *o*-diazo-toluene-azo-toluene or by boiling its acetic acid solution, N_2 being evolved.—3. Together with an amido-phenol or diamine by reducing with $SnCl_2$ the azo compounds obtained by combining *o*-diazo-toluene-azo-toluene with phenols or amines (Zincke a. Lawson, *B.* 19, 1455; 20, 1178).

Properties.—Thin colourless plates. Sol. benzene, hot alcohol, and hot HOAc. Not attacked by hot Ac_2O, cold H_2SO_4, or reducing agents.

AZINES. Compounds of the type $X''\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle Y''$. Thus, phenazine may be represented by the formula



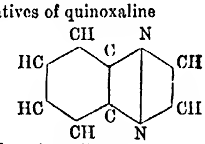
or $C_6H_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_6H_4$,

and the nomenclature of other azines may be gathered from two examples (Hinsberg, *B.* 20, 21).

Phen-naphthazine $C_6H_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_{10}H_6$.

Tolu-naphthazine $C_7H_6\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_{10}H_6$.

Derivatives of quinoxaline



are called quinoxalines, *e.g.* tolu-quinoxaline $C_7H_6\left\langle\begin{matrix}N-CH\\|\quad\|\\N-CH\end{matrix}\right.$, and naphtho-quinoxaline,

$$C_{10}H_6\left\langle\begin{matrix}N-CH\\|\quad\|\\N-CH\end{matrix}\right.$$

Formation.—1. From *o*-diamines and *o*-quinones or *o*-di-oxy- compounds.—2. By oxidation of a mixture of *o*-diamine and phenols (*e.g.* (β)-naphthol).—3. By boiling certain azo-dye-stuffs, derived from secondary amines, with dilute acids; *e.g.* sulpho-benzene-azo-phenyl-(β)-naphthyl-amine yields naphtho-phenazine and sulphanilic acid $C_6H_4(SO_3H)\,N_2.C_{10}H_6.NHC_6H_5 = C_{10}H_6\left\langle\begin{matrix}N\\N\end{matrix}\right\rangle C_6H_4 + C_6H_4(SO_3H).NH_2$ (Witt, *B.* 20, 571).—4. By fusing *o*-quinones with ammonium acetate, or by heating them with alcoholic NH_3 (Japp, *C. J.* 51, 100).

Properties.—Weak crystalline bases; their salts being decomposed by water. Reduced by $SnCl_2$ to hydrides, $R\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle R'$, whence Fe_2Cl_6 regenerates the original azine.

Azine-ammonium bases. Compounds of the form $X''\left\langle\begin{matrix}N\\|\\NR(OH)\end{matrix}\right\rangle Y''$. They have also been called Azonium bases (Witt, *B.* 20, 1183), a term previously applied by Fischer to quaternary hydrazine derivatives.

AZINSUCCINIC ACID
$(CO_2H)_2C_2H_2:N.N:C_2H_2(CO_2H)_2$. Crystalline solid. Very soluble in water and alcohol. Not decomposed by acids or alkalis. The ethers of this acid are obtained by the spontaneous decomposition of the ethers of diazosuccinic acid $C_2H_2N_2(CO_2R)_2$ on keeping, half the nitrogen being evolved. $A^{iv}Ba_2$: sparingly soluble yellowish-white powder.

Tetra-methyl-ether $A^{iv}Me_4$: [150°]; silky white prisms; easily soluble in hot water and alcohol, sparingly in cold water, alcohol, and hot ether; not volatile with steam (Curtius a. Koch, *B.* 18, 1299).

AZO-ANILINE *v.* Amido-benzene-azo-aniline under Azo- COMPOUNDS.

AZO-BENZENE *v.* Benzene-azo-benzene under Azo- COMPOUNDS.

TRIAZO-BENZENE and its derivatives *v.* DIAZO-BENZENE IMIDE and its derivatives.

AZO-BENZOIC ACID *v.* Carboxy-benzene-azo-benzoic acid under Azo- COMPOUNDS.

AZO- COLOURING MATTERS.

History.—The series of compounds comprised under this class contains one or more diatomic groups ·N:N· linking together acid or basic aromatic radicles. Of a very large number of azo-compounds known to science only a certain proportion are of technical value, and these are manufactured in large quantities owing to their importance as colouring matters. The first azo- compound introduced into commerce was the oxalate of amidoazobenzene ('aniline yellow,' *v.* benzene-azo-aniline), $C_6H_5.N_2.C_6H_4.NH_2$, manufactured in 1863 by the firm of Simpson, Maule & Nicholson, by the action of nitrous gas on aniline dissolved in alcohol. Three years later triamidoazobenzene, $NH_2.C_6H_4.N_2.C_6H_3(NH_2)_2$ (*v.* Amido-benzene-azo-phenylene-diamine under Azo- COMPOUNDS), was manufactured at Manchester and introduced under the name of 'Manchester brown' ('Bismarck brown,' 'Phenylene brown,' 'Vesuvine'). This compound was prepared by the action of nitrous acid upon *m*-phenylene-diamine. In 1875 diamidoazobenzene, $C_6H_5.N_2.C_6H_3(NH_2)_2$ (*v.* Benzene-azo-phenylene-diamine), was discovered independently by Caro and Witt (*B.* 10, 213, 350) and introduced into commerce by the latter under the name of 'chrysoïdine.' These basic colouring-matters were soon followed by acid azo- compounds of greater technical value (*B.* 10, 1378, 1509), and numerous patents have since that time been taken out, the general mode of preparation being similar in principle to that first employed in 1870 by Kekulé and Hidegh (*B.* 3, 233). These are the chief points in the industrial history of these compounds; the chemical history will be referred to under the individual compounds. Azobenzene, $C_6H_5.N_2.C_6H_5$ (*v.* Benzene-azo-benzene), which may be regarded as the prototype of the azo- compounds, has been known since 1834 (Mitscherlich, *A.* 12, 311), but the industrial development of these products is largely due to the researches of Griess upon the diazo- compounds (*A.* 106, 123; 113, 201; 117, 1; 120, 125; 121, 257; 137, 39). The theoretical views which have led to the adoption of the formulæ at present generally received have been developed chiefly by Kekulé (*Z.* 1866, 2, 309, 689).

Formation.—1. Compounds of the azobenzene type are produced by the action of mild reducing agents, such as alcoholic potash, alcoholic KOH and zinc dust, iron and acetic acid, or sodium stannite, upon the corresponding nitro-bodies: $2C_6H_5.NO_2 + 4H_2 = C_6H_5.N_2.C_6H_5 + 4H_2O$.

2. By the oxidation of the corresponding amido-derivatives by potassium permanganate, bleaching powder, chromic acid, hydric peroxide, &c., thus: $2C_6H_5.NH_2 + O_2 = C_6H_5.N_2.C_6H_5 + 2H_2O$ (Glaser, *Z.* [2] 2, 308). This method is applicable to the sulphonic acids and other derivatives of the amido- compounds: $2C_6H_3(CH_3)HSO_3.NH_2 + O_2 = N_2(C_6H_3.CH_3.HSO_3)_2 + 2H_2O$ [illustrating the production of azotoluenedisulphonic acid from toluidinesulphonic acid; Kornatzki, *A.* 221, 179].

3. By the action of ethyldichloramine (Tscherniak, *B.* 9, 147) upon certain aromatic amines (*e.g.* *p*-toluidine): $2C_7H_7.NH_2 + C_2H_5.NCl_2 = C_2H_5.NH_2HCl + HCl + C_7H_7.N_2.C_7H_7$ (Pierson a. Heumann, *B.* 16, 1048).

4. By the action of nitroso- compounds upon amines and phenols: $C_6H_5.NO + H_2N.C_6H_5 = C_6H_5.N_2.C_6H_5 + H_2O$ (production of azobenzene from nitrosobenzene and aniline; Baeyer, *B.* 7, 1638). Similarly $HO.C_6H_4.NO + H_2N.C_6H_5 = HO.C_6H_4.N_2.C_6H_5 + H_2O$ (production of benzene-azophenol from nitrosophenol and aniline; Kimich, *B.* 8, 1026). According to Henriques, substituted amidoazo-compounds are produced by the action of ethyl-β-naphthylnitrosamine upon aniline, &c.: $N(C_{10}H_7)Et.NO + H_2N.C_6H_5 = N(C_{10}H_7)Et.(N_2.C_6H_5) + H_2O$. The diazo- compound immediately becomes transformed into the isomeric benzeneazo-ethyl-β-naphthyl-amine, $C_6H_5.N_2.C_{10}H_6.NH.Et$ (*B.* 17, 2668, *v.* also O. N. Witt, *B.* 10, 1309). Amidoazobenzene reacts in a similar manner with the same nitrosamine forming $C_6H_5.N_2.C_6H_4.N_2.C_{10}H_6.NH.Et$.

5. From azoxy-compounds by intramolecular transposition, such as the formation of oxy-azobenzene (benzene-azo-phenol) by warming azoxybenzene with strong sulphuric acid
$\begin{matrix}C_6H_5.N\\C_6H_5.N\end{matrix}\!\!>\!O = C_6H_5.N_2.C_6H_4.OH$ (Wallach a. Belli, *B.* 13, 525).

6. By the action of phenylhydrazine upon the naphthoquinones: $C_{10}H_6O_2 + H_2N.NH.C_6H_5 = C_{10}H_6\!<\!\begin{matrix}O\\N-NH.C_6H_5\end{matrix} + H_2O$. The naphthoquinonehydrazide then undergoes intramolecular transposition with the formation of an azo-compound: $HO.C_{10}H_6.N:N.C_6H_5$. The compound thus obtained from (*e*)-naphthoquinone is identical with benzene-azo-(α)-naphthol, while (β)-naphthoquinone gives a compound which is isomeric and not identical with benzene-azo-(β)-naphthol (Zincke a. Bindewald, *B.* 17, 3026).

Preparation.—The method in general use for the preparation of azo- colours is that depending upon the readiness with which diazo- compounds react with amines and phenols. In practice it is not necessary to isolate the diazo- salt, but the amido- compound which is to be converted into a diazo- salt is treated with the necessary quantity of sodium nitrite and acid to diazotise the NH_2 group, and the solution of the diazo- salt is then mixed with the solution of the amine in acid or the phenol dissolved in alkali. During the process of diazotising, the solution containing the amido-compound must be kept well cooled, as the diazo- salts are very unstable,

especially in aqueous solution. Most aromatic amido- compounds lend themselves to this reaction, the azo- colours of commerce being produced by the action of diazotised amines, amido-sulphonic acids, or amido-carboxylic acids, upon amines, phenols, amido-sulphonic and oxy-sulphonic acids. A selection of typical reactions illustrating the formation of these compounds by the present method may be here conveniently discussed:

(*a*) When a salt of diazobenzene acts upon aniline the first product of the reaction is always diazobenzeneanilide (diazoamidobenzene): $C_6H_5.N_2.Cl + C_6H_5.NH_2 = C_6H_5.N_2.NH.C_6H_5 + HCl$. The latter compound was first produced by the action of nitrous gas upon aniline dissolved in cold alcohol (Griess, *A.* 121, 258). When allowed to stand in the presence of aniline and aniline hydrochloride, or when acted upon by hydrochloric acid or unstable metallic chlorides in the cold, the diazobenzeneanilide is slowly converted into the isomeric amidoazobenzene, $C_6H_5.N_2.C_6H_4.NH_2$. This last compound is manufactured on a commercial scale for the preparation of other azo- colours and the indulines (*q. v.*). In the case of other amines in which the para- position with respect to the NH_2 group is open (or the ortho- position in the naphthalene series), the transformation of diazo- into amidoazo- compounds takes place with great readiness. Thus, by the action of nitrous acid upon *o*- and *m*- toluidine, *m*-xylidine and the naphthylamines, amidoazo- compounds are at once formed.

(*b*) The salts of the aromatic diazo- compounds react with primary and secondary monamines, but not with tertiary monamines of the fatty series. The resulting products are diazo-compounds, such as $C_6H_5.N_2.NH.C_2H_5$ (diazobenzene-ethylamide) and $C_6H_5.N_2.N(CH_3)_2$ (diazobenzenedimethylamide). The diazo- compounds of this class do not furnish isomeric azo- compounds (Baeyer and Jäger, *B.* 8, 148). True azo- compounds of a mixed aromatic and fatty type are produced by the action of diazo-compounds upon the sodium derivatives of nitro-hydrocarbons of the fatty series, *e.g.*

$$C_6H_5.N_2.NO_3 + NaC_2H_4.NO_2 = C_6H_5.N_2.C_2H_4.NO_2 + NaNO_3$$

(formation of benzeneazonitroethane, V. Meyer and pupils, *B.* 8, 751, 1073, 1078; 9, 384; 12, 2285).

(*c*) Diazo-compounds always furnish true azo-compounds with secondary and tertiary aromatic monamines, such as $C_6H_5.N_2.C_6H_4.NMe_2$ (benzene-azo-dimethylaniline) by the action of diazobenzene upon dimethylaniline (Griess, *B.* 10, 528), and $C_6H_5.N_2.C_6H_4.NH.C_6H_5$ (benzene-azo-diphenylamine) by the action of diazobenzene upon diphenylamine (Witt, *B.* 12, 259, and *C. J.* 35, 185).

(*d*) The action of diazo- compounds upon aromatic diamines is typified by the action of diazobenzene-chloride upon *m*-diamidobenzene to produce chrysoïdine: $C_6H_5.N_2.Cl + C_6H_4(NH_2)_2 = C_6H_5.N_2.C_6H_3(NH_2)_2.HCl$. Nitrous acid gives with ortho-diamines a class of substances termed by Griess azimido- compounds:

$$C_6H_4(NH_2)_2 + HNO_2 = C_6H_4{<}{\genfrac{}{}{0pt}{}{N}{N}}{>}NH + 2OH_2$$

(Hofmann, *A.* 115, 249; Ladenburg, *B.* 11, 219; Rudolph, *B.* 12, 1296; Griess, *B.* 15, 1878). Metadiamines give under the same circumstances compounds of the type of triamidoazobenzene (Bismarck brown) $2C_6H_4(NH_2)_2 + HNO_2 = (NH_2)C_6H_4.N_2.C_6H_3(NH_2)_2 + 2H_2O$ (Caro a. Griess *Z.* 1867, 278). By acting with an excess of HNO_2 upon *p*- and *m*- $C_6H_4(NH_2)_2$ in acid solution with suitable precautions both these diamines can be diazotised and give azo- colours when combined with phenols (Griess, *B.* 17, 607 and 19, 317).

(*e*) The formation of azo- colours from diazo-compounds and phenols as illustrative of the general method of technical production is shown by the following typical examples: $C_6H_5.N_2.NO_3 + C_6H_5.ONa = C_6H_5.N_2.C_6H_4.OH + NaNO_3$ (benzeneazophenol from diazobenzene nitrate and sodium phenate: Kekulé and Hidegh, *B.* 3, 233). By a similar reaction would be formed such compounds as benzeneazoresorcin, $C_6H_5.N_2.C_6H_3(OH)_2$ (Typke, *B.* 10, 1576), benzene-azo-(α)-naphthol, $C_6H_5.N_2.C_{10}H_6.OH\alpha$, &c. (*ibid.* 1580). Azosulphonic acids are formed by the action of diazosulphonic acids upon phenols, or by the action of diazo- salts upon phenolsulphonic acids, thus, for example, *p*-sulphobenzene-azo-β-naphthol (Poirrier's 'Orange No. II.'), $HSO_3.C_6H_4.N_2.C_{10}H_6.OH\beta$ from diazo-benzene sulphonic acid and sodium (β)-naphtholate; benzene-azo-(β)-naphthol disulphonic acid, $C_6H_5.N_2.C_{10}H_4(HSO_3)_2.OH\beta$ from diazo-benzene and (β)-naphthol sodium disulphonate ('Orange G,' Meister, Lucius a. Brüning), or *p*-sulphobenzene-azo-(β)-naphthol disulphonic acid, $HSO_3.C_6H_4.N_2.C_{10}H_4(HSO_3)_2.OH\beta$ from diazotised sulphanilic acid and (β)-naphtholdisulphonic acid sodium salt (Meldola, *B.* 13, 942).

Classification and Nomenclature.—Azo- compounds may be described as primary, secondary, tertiary, &c. according as they contain 1, 2, 3, &c. N_2- groups. The modes of formation above described have been illustrated by reference to primary azo- compounds, all of which (with the exception of the mixed aromatic and fatty compounds) may be regarded as derivatives of azobenzene, $C_6H_5.N_2.C_6H_5$, benzeneazonaphthalene, $C_6H_5.N_2.C_{10}H_7$ and azonaphthalene, $C_{10}H_7.N_2.C_{10}H_7$, or generally, in the case of phenolic azo- compounds, as $R.N_2.Pl$, where R may stand for C_6H_5, $C_{10}H_7$, $C_6H_4.HSO_3$, $C_6H_4.NO_2$, &c., and Pl for $C_6H_4.OH$, $C_{10}H_6.OH$, $C_{10}H_5(HSO_3)OH$, &c. It will be found convenient to write the formulæ of azo- compounds so as to represent the order of introduction of the radicles. Thus, $C_6H_5.N_2.C_6H_4.OH$ indicates the product from diazobenzene and phenol, and would be described as benzene-azo-phenol; $C_6H_4(HSO_3)N_2.C_{10}H_6.OH\alpha$ is *p*-sulphobenzene-azo-(α)-naphthol, obtained by the action of diazotised-sulphanilic acid upon (α)-naphthol; while $C_6H_5.N_2.C_{10}H_5(HSO_3)OH\alpha$ is the isomeric benzene-azo-(α)-naphtholmonosulphonic acid obtained by the action of diazobenzene upon (α)-naphtholmonosulphonic acid. The same rules may be followed with the more complicated types of azo- compounds; thus, for instance $C_6H_5.N_2.C_6H_4.N_2.C_6H_3(OH)_2$, benzeneazobenzene-azoresorcin obtained by the action of diazotised amidoazobenzene upon resorcin; in like manner $C_6H_5.N_2.C_7H_6.N_2.C_6H_3(OH)_2$ maybe called benzene-azotoluene-azoresorcin by the action of diazotised

benzene-azoamidotoluene upon resorcin; and $C_6H_5.N_2.C_6H_2(OH)_2.N_2.C_6H_5$, benzeneazodioxybenzeneazobenzene by the successive introduction of two diazobenzene-groups into resorcin. Secondary and tertiary azo- compounds of the types $(R.N_2)_2Pl''$, and $(R.N_2)_3Pl'''$ have been termed by Wallach *disazo-* and *trisazo-* compounds (*B.* 15, 22 and 2812; *v.* also Heumann, *ibid.* 813).

Secondary and tertiary azo- compounds.—The typical secondary azo- compound of the type $(R.N_2)_2Pl''$ is the so-called 'phenolbidiazobenzene,' $(C_6H_5.N_2)_2:C_6H_3.OH$, discovered by Griess (*B.* 10, 628). Compounds of this class are formed by the successive introduction of two diazotised radicles into a phenol. The resorcin secondary azo- compounds have been especially studied by Wallach (*B.* 15, 22; Wallach a. B. Fischer, *ibid.* 2814), and the cresol compounds by Nölting a. Kohn (*B.* 17, 351). Analogous amido- compounds of the type $(R.N_2)_2:C_6H_2(NH_2)_2$ have been obtained by the introduction of diazotised radicles into chrysoïdine (Griess, *B.* 16, 2028). Secondary azo- compounds of the type $R''(N_2.Pl)_2$ have been obtained by Wallach by acetylating one amido- group in a diamine, diazotising the acetdiamido- compound, and combining with a phenol so as to produce a compound of the type $R''<\begin{matrix}N_2.Pl\\NH.Ac\end{matrix}$. The acetyl group is then removed, the NH_2-group diazotised, and the diazo-compound $R''<\begin{matrix}N_2.Pl\\N_2.Cl\end{matrix}$ again combined with a phenol (*B.* 15, 2825 and Wallach a. Schulze, *ibid.* 3020). The metadiamines appear to lend themselves most readily to this method. The most direct method of preparing secondary azo-compounds of this class is by diazotising both amido- groups in a *p*- or *m*-diamine, and then acting with the product upon a phenol or phenolsulphonic acid (Griess, *B.* 17, 607 and 19, 817). Another method of obtaining secondary azo- compounds of these types is by diazotising a *p*-nitramido- compound and combining with a phenol or secondary or tertiary amine so as to produce $NO_2.R''.N_2.Pl$ or $NO_2.R''.N_2.R''.NR_2$. The nitro- group is then reduced, the amido-azo-compound diazotised and again combined with a phenol, &c., thus producing $R''(N_2.Pl)_2$, $R''<\begin{matrix}N_2.R''.NR_2\\N_2.Pl,\end{matrix}$ &c. (Meldola, *C. J.* 43, 425; 45, 106 and 47, 657). If the nitro-azo- compound is combined with a monamine and the nitro-group reduced, a diamidoazo- compound of the type $NH_2.R''.N_2.R''.NH_2$ is produced in which both amido- groups can be diazotised and combined with phenols so as to form tertiary azo- compounds, $Pl.N_2.R''.N_2.R''.N_2.Pl$ (*ibid.*). Secondary azo- compounds of these types are also formed by reducing *p*-nitracetanilide, diazotising and combining with a phenol or amine so as to produce azo- compounds of the type $C_6H_4<\begin{matrix}NH.Ac.\\N_2.Pl\end{matrix}$. The acetyl group is then removed, the amido-azo- compound diazotised and again combined with a phenol (Nietzki, *B.* 17, 343 and 1350).

Secondary azo- compounds of the type $R'.N_2.R''.N_2.Pl$ are obtained by diazotising amido-azo- compounds and combining the diazo-azo-salt with phenols. The typical compound, **$C_6H_5.N_2.C_6H_4.N_2.C_6H_4.OH$, was first prepared by Caro and Schraube (*B.* 10, 2230) and several members of this group have since been introduced into commerce under the names of 'Biebrich scarlet,' 'Croceine scarlet,' &c. These scarlets are of considerable technical import**ance, especially the latter, which are prepared by the action of diazotised amidoazobenzene-sulphonic acid and its homologues upon (β)-naphthol-(α)-sulphonic acid. By the action of diazotised amidoazobenzene upon chrysoïdine a tertiary azo- compound of the type $\begin{matrix}R'N_2.R''.N_2\\R'.N_2\end{matrix}>C_6H_2(NH_2)_2$ is formed (Griess, *B.* 16, 2036). Secondary azo- compounds of some importance have recently been prepared by diazotising diamidodiphenyl (benzidine) and its homologues and combining the tetrazo-salt with phenols, amines, and their sulphonic acids; of these colouring matters 'Congo red,' $\begin{matrix}C_6H_4.N_2.C_{10}H_5(HSO_3)NH_2\alpha\\C_6H_4.N_2.C_{10}H_5(HSO_3)NH_2\alpha\end{matrix}$ may be mentioned as a typical example. Tertiary azo- compounds derived from triphenyl-carbinol are obtained by diazotising the rosanilines and combining with phenols (Meldola, *C. J.* 47, 668).

Constitution of Azo- compounds. When a diazo- compound combines with an amine or phenol to form an azo- compound the N_2-group invariably takes up the para- position with respect to the NH_2, NHR, NR_2, or HO, if this position is open. The proof of the constitution of azo- compounds is furnished by the products which they yield on complete reduction. Thus, amidoazobenzene, $C_6H_5.N_2.C_6H_4.NH_2$, gives on reduction aniline and *p*-phenylene-diamine; chrysoïdine gives aniline and (1, 2, 4)- triamidobenzene (Witt, *B.* 10, 658). The constitution of some of the azo- compounds obtained by combining diazosulphonic acids with phenols has been established by Griess (*B.* 11, 2191). The constitution of the azo-naphthol colours has been determined chiefly by Liebermann and his pupils (*B.* 14, 1310 and 1795; Jacobson, *ibid.* 1791; also Witt, *C. J.* 35, 179). When diazo-compounds act upon substituted phenols, such as salicylic acid, the N_2-group also takes up the para- position with respect to the HO-group (P. F. Frankland, *C. J.* 37, 746); thus (α)-naphthaleneazosalicylic acid gives on reduction α-$C_{10}H_7.NH_2$ and $C_6H_3(HO)(NH_2)CO_2H$ [1:4:2] When the para- position with respect to the NH_2 or HO-group is already occupied the N_2-group enters the ortho- position (Nölting a. Witt, *B.* 17, 77; Liebermann a. Kostanecki, *ibid.* 130, 876; Griess, *ibid.* 338; Nölting and Kohn, *ibid.* 351). This law holds good also when the para- position is occupied by an azo-group, as in the formation of $(C_6H_5.N_2)_2:C_6H_3.OH$ from benzeneazophenol by the introduction of another $C_6H_5.N_2$-group (Nölting a. Kohn, *B.* 17, 368). In the case of the (β)-naphthalene derivatives the N_2-group also enters the ortho-(α)-position with respect to the hydroxyl or amidogen group. Thus (β) - naphthol orange, $HSO_3.C_6H_4.N_2.C_{10}H_6.OH$, gives on reduction sulphanilic acid and (α)-amido-(β)-naphthol, the latter yielding (β)-naphthoquinone on oxidation (Liebermann, *B.* 14, 1310). Similarly the azo-derivatives of (β)-naphthylamine yield *o*-diamido-naphthalene ($NH_2:NH_2 = \alpha_1:\beta_1$) on reduction

(Lawson, *B.* 18, 796 and 2422). The fact that such compounds as benzeneazo-(β)-naphthol are insoluble in cold aqueous alkalis has led Liebermann to the suggestion that these compounds no longer contain HO, but possess the formula $C_6H_5.N\!<\!{}^{NH}_{O}\!>\!C_{10}H_6$ (*B.* 16, 2858). A similar conclusion has been suggested by Meldola with respect to the (β)-naphthylamine derivatives, for which he proposes the formula $R.N\!<\!{}^{NH}_{NH}\!>\!C_{10}H_6$, thus indicating a relationship to the azimido-compounds above referred to (*C. J.* 45, 117). This conclusion is supported by the investigations of Zincke and his pupils (*B.* 18, 3125, 3132 and 3142). This author has shown that these (β)-naphthalene, as well as other ortho-amidoazo- compounds, can be oxidised to compounds of the azimido- type, $R.N\!<\!\overset{N}{\underset{N}{|}}\!>\!C_{10}H_6$, and he suggests for them the alternative formula $\begin{matrix} HN \\ | \\ R.NH.N \end{matrix}\!>\!C_{10}H_6$. According to a recent paper by Nietzki a. Goll (*B.* 19, 1281) it appears, however, that amidoazo-(β)-naphthalene contains an NH_2-group, or at any rate can be diazotised under certain conditions. There can be no doubt that the question of the constitution of the azo- compounds is much more complicated than was at first supposed, since by the action of diazo- compounds upon phenols two isomeric azo- compounds may be formed at the same time, the isomerism probably depending upon the position of the $R.N_2$-groups with respect to the HO as well as upon the formation of bodies of the oximido- type. This appears to be the case especially with the azo- derivatives of resorcinol (Wallach, *B.* 15, 22 and 2811).

General properties and technology.– The individual azo- colours will be described under their respective headings, so that it will be only necessary here to give a brief account of the general characters of these colouring matters. The parent azo- compounds, $C_6H_5.N_2.C_6H_5$, $C_6H_5.N_2.C_{10}H_7$, $C_{10}H_7.N_2.C_{10}H_7$, although possessed of colour are not of any value as dyestuffs: it is only when acid or basic radicles are present in one or both aromatic nuclei that true colouring matters are formed. The colours produced by these compounds are of various shades of yellow, orange, brown, red, scarlet, indigo-blue and violet. No pure blue or green azo-compound is known. Of the basic primary azo-compounds, amidoazo-benzene, chrysoidine, and 'phenylene brown,' show a gradation in shade from yellow through orange to brown. The two last compounds are now alone of technical value. Among the acid azo- colours a regular gradation of shade is also observed with the increase in molecular weight. This is well seen in the colours produced by the action of diazo-benzene and its homologues upon the naphtholsulphonic acids, the lowest members of the series being orange, and the highest members scarlet of an increasing shade of blueness. The acid primary azo- compounds are dyed from acid baths and have great affinity for silk and wool, but do not readily dye cotton without the use of mordants. Primary azo- colours as a rule dissolve in strong sulphuric acid with a red or orange colour. Azo- colours can be produced directly in the fibre of cotton by impregnating the latter with a phenol and a diazo- compound, and then developing by means of an acid (T. Holliday, *S. C. I.* 4, 204). A similar process has been described by Grässler (*S. C. I.* 4, 262) who uses the nitrite in the form of an ammonium salt or in combination with ammonium salts, so that on heating the impregnated fabric the nitrous acid is liberated in the presence of the amine and phenol, and the colour is developed without the use of acid. Oxyazo-compounds, which are not sulphonic acids, and which are insoluble, can be made soluble by warming them in aqueous or alcoholic solutions of bisulphites. A soluble double compound is thus formed which is decomposed on heating with the liberation of the colouring matter so that the process is especially applicable for calico printing (Meister, Lucius a. Brüning, *B.* 17, 452). The secondary azo-colours derived from diazotised amidoazobenzene and its homologues in combination with naphtholsulphonic acids are scarlets of greater tinctorial power and purity than the primary azo- scarlets, and possess a certain affinity for cotton, especially the 'croceine scarlets' already referred to. The secondary azo- colours derived from diazotised benzidine ('Congo red' series) and its homologues are reds or yellows which also possess a certain affinity for cotton, but many of these colours are too sensitive to acids to be of much use technically. The stability of these colours is increased, however, by using the higher homologues of benzidine. It is only among secondary azo- compounds that true shades of violet and indigo blue are found (Nietzki, *B.* 17, 344; Meldola, *C. J.* 47, 665). Some of these blue shades are now met with in the market, a typical compound of the class being a salt of ditolyltetrazo-(β)-naphtholdisulphonic acid,

$$\begin{matrix} C_7H_6.N_2.C_{10}H_5(HSO_3)(OH)\beta \\ C_7H_6.N_2.C_{10}H_5(HSO_3)(OH)\beta \end{matrix}$$ (Azo - blue of F. Bayer & Co.). Secondary azo- compounds dissolve as a rule in strong sulphuric acid with a violet, blue, or green colour. The tertiary azo-compounds have but little tinctorial value. For observations on the absorption spectra of azo-colours see papers by H. W. Vogel (*B.* 11, 623), Landauer (*B.* 14, 391), and Stebbins (*Am.* 6, 117 and 149). R. M.

AZO-COMPOUNDS. (*V. also* AZO- COLOURING MATTERS and DI-AZO- COMPOUNDS.) The nomenclature of these compounds is based on the following rules. Imagine N_2 displaced by H_2 and the compound to break up accordingly, one H going to one half and one to the other. If both the resulting compounds are aromatic, name the compound richest in carbon according to the rules followed in this dictionary, and prefix azo- to the name. Before azo- write the name of the hydrocarbon from which the other half of the molecule is derived. Then prefix all the substituents of the latter so that they may follow one another in this order: chloro-, bromo-, iodo-, cyano-, nitro-, oxy-, amido-, sulpho-, and carboxy-. When both halves of the azo- compound contain the same number of atoms of carbon, then the half which contains CO_2H is put last. If neither contain CO_2H, the one containing

SO_3H comes last; if neither contain this, preference is given to OH, NH_2, NO_2, Br, or Cl, in succession.

If one half of an azo- compound is derived from a fatty hydrocarbon the name of this half is written last.

The compounds obtained by the action of diazo- compounds upon (β)-naphthylamine, (β)-naphthol, or more generally upon amido- or oxy-compounds in which the *p*-position is already occupied, are described as if they were ordinary azo- compounds. It is, however, not improbable that they may have a different constitution. Thus the compounds obtained from diazo- compounds and (β)-naphthylamine behave like diazoamides in their decomposition by acids into (β)-naphthylamine, a phenol, and nitrogen; but act on reduction like amido-azo-derivatives giving (1:2)-naphthylene-diamine and the amine. Three views may be taken with regard to the constitution of these bodies:—(1) That they are true diazoamides; (2) that they are *o*-amido-azo- derivatives; (3) that they are hydrazimido- compounds, *i.e.* dihydrides of azimido- compounds.

The first hypothesis easily explains their decomposition by acids; and their reduction to naphthylene-diamine might be accounted for by assuming an intermediate change into the amido-azo- compound. However, the fact that a different isomeric body is formed by diazotising (β)-naphthylamine and combining it with the other amine does not agree with this view, since compounds of the form $X.N_2.NHY$ and $Y.N_2.NHX$ are always found to be identical. The other reactions of these bodies are also inconsistent with this hypothesis. The hypothesis that the compounds are *o*-amido-azo- derivatives does not readily account for their behaviour on oxidation, which tends to show that they do not contain an NH_2 group.

The third hypothesis leads to the formula

$$C_{10}H_6\left\langle\begin{array}{l}NH\\ |\\ N.NHR\end{array}\right. \quad\text{or}\quad C_{10}H_6\left\langle\begin{array}{c}NH\\ NH\end{array}\right\rangle NR.$$

It is strongly supported by the fact that on oxidation these bodies give rise to white crystalline azimido- compounds, which probably have the constitution $C_{10}H_6\left\langle\begin{array}{c}N\\ |\\ N\end{array}\right\rangle NR$, analogous to Griess's azimidobenzene $C_6H_4\left\langle\begin{array}{c}N\\ |\\ N\end{array}\right\rangle NH$ obtained by the action of nitrous acid on *o*-phenylene-diamine. The corresponding compounds from (β)-naphthol and diazo-salts may also be obtained by the action of hydrazines upon (β)-naphthoquinone, and hence may be represented in a similar manner by the formulæ

$$C_{10}H_6\left\langle\begin{array}{l}O\\ |\\ N.NHR\end{array}\right. \quad\text{or}\quad C_{10}H_6\left\langle\begin{array}{c}O\\ NH\end{array}\right\rangle NR.$$

The formation of hydrazimido- compounds from a diazo- salt and (β)-naphthylamine can be explained by assuming the intermediate formation of true diazo-amides $C_{10}H_7.NH.N{:}NR$, which by taking up H_2O (or HCl) would form $C_{10}H_7.NH.N(OH).NHR$ or $C_{10}H_7.NH.NH.N(OH)R$, and by again eliminating H_2O it might give the hydrazimido- compound. The decomposition by acids might also be explained as a change inverse to the above, resulting in the formation of the diazo-amide, which would then be decomposed. The *ortho*-amido-azo- derivatives of the benzene series would also seem to be similarly constituted, for on oxidation they also give colourless crystalline azimido- compounds.

Apparently opposed to the hydrazimido-hypothesis, is the behaviour of these bodies towards nitrous acid, which converts them into diazo- compounds. In many points, however, these diazo-compounds greatly differ from the ordinary diazo- compounds, and their constitution may possibly be expressed by the formula: $R'\left\langle\begin{array}{l}N.N.OH\\ |\quad |\\ N.N.R'\end{array}\right.$, which would represent their formation from hydrazimido- compounds. By $SnCl_2$ or SO_2 these diazo- compounds are not reduced to hydrazines but to non-basic stable bodies which probably have the constitution $R''\left\langle\begin{array}{l}N—NH\\ |\quad\ |\\ N—N.R'\end{array}\right.$. The *o*-diazo-imides readily lose N_2 on heating and are converted into azimido-compounds $R''\left\langle\begin{array}{c}N\\ |\\ N\end{array}\right\rangle N.R'$ identical with those obtained by oxidation of the *o*-amido-azo- compounds. On the hydrazimido- hypothesis the body derived from diazo-benzene and phenyl-(β)-naphthylamine would be represented by the formula $C_{10}H_6\left\langle\begin{array}{l}N.C_6H_5\\ |\\ N_2HC_6H_5\end{array}\right.$ which agrees with its reactions. Thus conc. HCl removes aniline, forming an azine $C_{10}H_6\left\langle\begin{array}{c}N\\ |\\ N\end{array}\right\rangle C_6H_4$, while oxidising agents produce a powerful ammonium base $C_{10}H_6N_3(C_6H_5)_2OH$ (Meldola, *C. J.* 45, 107; Nölting a. Wilt, *B.* 17, 77; Lawson, *B.* 18, 796, 2422; Sachs, *B.* 18, 3125; Zincke, *B.* 18, 3132, 3142; Zincke a. Lawson, *B.* 19, 1452).

Description of Azo- compounds.

Acetophenone-azo-(β)-naphthol [4:1] $C_6H_4(CO.CH_3)—N_2—C_{10}H_6(OH)$. Formed by diazotising *p*-amido-acetophenone and combining the diazo- compound with (β)-naphthol in alkaline solution (Klingel, *B.* 18, 2695). Slender red needles. V. sol. alcohol, sl. sol. ether, insol. water. Dyes silk a dull red.

***o*-Amido-benzene-azo-aceto-acetic acid** $C_6H_4(NH_2)—N_2—CH(CO.CH_3).CO_2H$. [157°]. Orange-red tables. Easily soluble in acetic acid, alcohol, ether and chloroform, sparingly in water. Formed by reduction of *o*-nitro-benzene-azo-aceto-acetic acid with $FeSO_4$ and NH_3 (Bamberger, *B.* 17, 2420).

***p*-Amido-benzene-*p*-azo-aniline** $C_6H_4(NH_2)—N_2—C_6H_4(NH_2)$. ***p*-Azo-aniline. Di-*amido-azo-benzene*.** [235°]. Long flat yellow needles. Easily soluble in alcohol, sparingly in benzene and ligroine.

Preparation.—1. The mono-acetyl derivative of *p*-phenylene-diamine is diazotised and combined with aniline, the anilide thus obtained is dissolved in aniline and warmed with aniline hydrochloride by which it is converted into the mono-acetyl derivative of amido-benzene-azo

aniline, which is finally saponified.—2. From its di-acetyl derivative which is formed by the action of zinc and ammonia on acetyl-p-nitro-aniline (Mixter, *Am.* 5, 282).

The mono-acid salts are green, the di-acid red. $B''H_2Cl_2$: needles.

Mono-acetyl derivative $C_{12}H_8N_2(NH_2)(NHAc)$. [212°], glistening golden yellow plates. Its salts are red (Nietzki, *B.* 17, 345).

Di-acetyl derivative [282°] (M.).

Amido-benzene-azo-aniline
[4:1] $C_6H_4(NH_2)—N_2—C_6H_4NH_2$ [1:4]. [142°]. Obtained by reducing nitro-benzene-azo-nitro-benzene [206°] with alcoholic ammonium sulphide (Janovsky, *M.* 6, 460). Minute plates (from alcohol). Salt.—$B''H_2Cl_2$. This body is probably identical with the preceding, the melting-point having perhaps been misprinted.

***m*-Amido-benzene-*m*-azo-aniline**
[3:1]$C_6H_4(NH_2)-N_2-C_6H_4(NH_2)$ [1:3]. From the nitro-compound by ammonium sulphide (Janovsky, *M.* 6, 458). Minute flat yellow needles with green lustre (from alcohol).

Amido-benzene-azo-benzene-*p*-sulphonic acid
[4:1] $C_6H_4(HSO_3)-N:N-C_6H_4.NH_2$ [1:4] S. ·0144 at 22°. Yellowish-white microscopic needles or scales (containing aq). Nearly insoluble in water, alcohol, ether, and chloroform. Formed by the action of diazo-benzene-*p*-sulphonic acid on aniline (to extent of about 30 p.c.). Prepared from benzene-azo-aniline and fuming H_2SO_4 at about 70°. On reduction with tin and HCl it gives *p*-phenylene-diamine and sulphanilic acid.

Salts.—$A'NH_4$*: orange-yellow plates.—A'_2Ba 6aq: sparingly soluble trimetric orange needles—A'_2Ca 2aq (Griess, *B.* 15, 2184).

Amido-benzene-azo-benzene-*p*-sulphonic acid
[4:1]$C_6H_4(SO_3H)-N:N-C_6H_4.NH_2$[1:4]. S. ·0196 at 22°. Pearly plates (containing aq). Formed by reduction of the sparingly soluble nitro-benzene-azo-benzene-*p*-sulphonic acid with ammonium sulphide. On complete reduction with tin and HCl it gives *p*-sulphanilic acid and *p*-phenylene-diamine, and hence ought, according to theory, to be identical with the preceding compound; this, however, does not appear to be the case.

Salts.—KA'aq: yellow trimetric plates.—*NaA': needles.—BaA' 6aq: large glistening monoclinic needles.—CaA' 4aq: yellow pearly plates.—PbA'_2: monoclinic plates (Janovsky, *B.* 16, 1488; *M.* 4, 279, 652).

Di-amido-benzene-azo-benzene-*p*-sulphonic acid $(NH_2)_2C_6H_3-N_2-C_6H_4.SO_3H$. *Chrysoïdine sulphonic acid.* Brownish-red glistening needles. Sl. sol. water.

Formation.—1. By combination of *p*-diazo-benzene-sulphonic acid with *m*-phenylene di-amine.—2. By sulphonation of chrysoïdine. On reduction it gives sulphanilic acid and (1:2:4)-tri-amido-benzene (Griess, *B.* 15, 2196).

***m*-Amido-benzene-*p*-azo-di-methyl-aniline**
[3:1] $C_6H_4(NH_2)—N_2—C_6H_4NMe_2$ [1:4]. [166°]. Golden laminæ, sol. alcohol. Formed by the action of warm dilute H_2SO_4 on its acetyl derivative [184°] which is obtained by mixing diazotised acetyl-*m*-tolylene-diamine with dimethyl-aniline (Wallach, *A.* 234, 263).

***p*-Amido-benzene-azo-dimethylaniline**
[4:1] $NH_2.C_6H_4.N_2.C_6H_4.NMe_2$ [1:4]. [183°]. By warming the alcoholic solution of the nitro-compound $NO_2.C_6H_4.N_2.C_6H_4.NMe_2$ with ammonic sulphide (Meldola, *C. J.* 45, 107).

Properties.—Brick-red needles (from dilute alcohol). Insol. boiling water, but forms yellow solutions in most solvents. Reduced by zinc dust and HCl it gives dimethyl-*p*-phenylene-diamine and *p*-phenylene-diamine. On adding acetic acid to an alcoholic solution, the liquid turns green, on dilution with water it becomes red. In conc. H_2SO_4 the solution is orange. A very dilute solution mixed with nitrous acid and exposed to the air turns blue (test for nitrous acid).—$B''(HCl)_2PtCl_4$.

Methylo-iodide.—Insoluble brown scales.

Acetyl derivative.—Orange needles (from alcohol). [217°].

***p*-Amido-benzene-azo-(β)-naphthol**
[4:1] $NH_2.C_6H_4.N:N.C_{10}H_6.OH$ [α:β]. Formed by reducing the corresponding nitro-compound with ammonium sulphide and ammonia. Forms a crimson solution in H_2SO_4 (Meldola, *C. J.* 47, 663).

***p*-Amido-benzene-azo-(α)-naphthol**
[4:1] $NH_2.C_6H_4.N_2.C_{10}H_6.OH$ [α:β]. Formed by reducing para-nitro-benzene-azo-(α)-naphthol in hot dilute NaHO with ammonium sulphide; ppd. by HCl (Meldola, *C. J.* 47, 662). Dark brown powder; sl. sol. hot water, v. sol. hot alcohol. Forms a red solution in conc. H_2SO_4.

***p*-Amido-benzene-azo-(β)-naphthol di-sulphonic acid.** *Acetyl derivative*
$C_6H_4(NHAc)-N_2-C_{10}H_4(OH)(SO_3H)_2$. Golden glistening plates. Scarlet red dye-stuff. Formed by diazotising the mono-acetyl derivative of *p*-phenylene-diamine and combining it with (β)-naphthol (R)-di-sulphonic acid (modification insoluble in alcohol). By saponification of the acetyl group it yields a bordeaux-red dye stuff. By diazotising the latter and combining it with (β)-naphthol di-sulphonic acid a blue colouring matter is produced (Nietzki, *B.* 17, 344).

***p*-Amido-benzene-azo-(α)-naphthylamine**
[4:1]$NH_2.C_6H_4.N_2.C_{10}H_6NH_2$[1:4]. [160°]. Formed by reducing $NO_2.C_6H_4.N_2.C_{10}H_6.NH_2$ with aqueous ammonic sulphide (Meldola, *C. J.* 43, 432). Ochreous needles. Readily soluble in alcohol, acetone, benzene and chloroform. Its salts form crimson aqueous solutions; excess of acid throws down the neutral salts.—$B''(HCl)_2PtCl_4$.

***p*-Amido-benzene-azo-*o*-oxy-benzoic acid**
[4:1] $NH_2.C_6H_4—N_2—C_6H_3(OH)(CO_2H)$ [1:4:2]. From the sodium salt of *p*-nitro-benzene-azo-salicylic acid by reduction with ammonium sulphide. Colourless needles. Sl. sol. boiling water. Its alkaline solutions are yellow. Glacial HOAc forms a crimson solution. Blackens at 219°-220° C. (Meldola, *C. J.* 47 667).

***m*-Amido-benzene-azo-phenol**
[3:1] $C_6H_4(NH_2)-N_2—C_6H_4.OH$ [1:4].
[168°]. Brownish yellow scales. Obtained by saponification of the acetyl derivative.

Acetyl derivative
$C_6H_4(NHAc).N_2.C_6H_4OH$ [c. 208°]. Prepared by diazotising the mono-acetyl derivative of *m*-phenylene-diamine and combining it with phenol. (Wallach, *B.* 15, 3020).

***p*-Amido-benzene-azo-phenol**
[4:1] $NH_2.C_6H_4.N:N.C_6H_4.OH$ [1:4]. [181°]. Obtained by heating *p*-nitro-benzene-azo-phenol with ammonium sulphide. Brown scales (from

water); v. sol. alcohol.—$B'_2H_2PtCl_6$ (Meldola, *C. J.* 47, 658).

p-Amido-benzene-azo-diphenylamine

[4:1] $NH_2.C_6H_4.N_2.C_6H_4NHC_6H_5$ [1:4] [c. 91°]. Got by reducing the nitro- compound by ammonic sulphide (Meldola, *C. J.* 43, 440).

Properties.—Sl. sol. in boiling water, v. sol. alcohol, acetone, chloroform and benzene, forming yellow solutions. HCl added to the alcoholic solution turns it first green, then red. Solution in conc. H_2SO_4 is violet, turned red by diluting.

Salts.—Form crimson aqueous solutions. Dye wool orange.

m-Amido-benzene-azo-m-phenylene-diamine

[3:1] $C_6H_4(NH_2)—N_2—C_6H_3(NH_2)_2$ [1:2:4]. *Bismarck brown.* [137°]. Ppd. by adding $NaNO_2$ to a neutral solution of *m*-phenylene-diamine hydrochloride (Caro a. Griess, *Z.* 1867, 278). Brown plates. Sl. sol. in hot water; v. e. sol. alcohol and ether. Dyes wool brown. Absorption spectrum (Hartley, *C. J.* 51, 180).

Salts.—$B''2HCl$.—$B''H_2PtCl_6$.

p-Amido-benzene-azo-phenylene-diamine

*[4:1] $C_6H_4(NH_2)—N_2—C_6H_3(NH_2)_2$ [1:2 or 3:4]. From benzene-azo-benzene by nitration and reduction (Janovsky, *M.* 6, 466).

p-Amido-benzene-azo-resorcin

[4:1] $NH_2.C_6H_4.N:N.C_6H_3(OH)_2$.[1:2:4]. By dissolving *p*-nitro-benzene-azo-resorcin in dilute NaHO and warming with ammonium sulphide (Meldola, *C. J.* 47, 661). Its alkaline solutions are red; its acid solutions are pale orange.—$B'_2H_2SO_4$: silvery scales.—$B'_2H_2PtCl_6$.

p-Amido-benzene-azo-m-xylidine

[4:1] $NH_2.C_6H_4.N_2.C_6H_2Me_2NH_2$ [1:3:5:2] [163°]. Formed by reducing $NO_2.C_6H_4.N_2.C_6H_2Me_2NH_2$ with aqueous ammonic sulphide (Meldola, *C. J.* 43, 432). Golden scales (from water). V. sol. alcohol and benzene.

Salts.—The acid salts are very soluble in water. Excess of HCl forms an amorphous brown pp. of $B''2HCl$.—$(B''2HCl)PtCl_4$.

Amido-thiophene-azo-benzene

$C_6H_5.N_2.C_4SH_2.NH_2$. Formed by adding diazobenzene chloride to a tolerably concentrated solution of thiophenine hydrochloride.—$B'HCl\frac{1}{2}aq$: yellow needles, soluble in water and alcohol (Stadler, *B.* 18, 2317).

Amido-thiophene-azo-benzene-p-sulphonic acid [4:1] $C_6H_4(SO_3H).N_2.C_4SH_2.NH_2$. Formed by combination of diazo-benzene-*p*-sulphonic acid with thiophenine. Yellow needles, red when dry. Sl. sol. water and alcohol. Dyes silk yellow. (Stadler, *B.* 18, 2318).

Amido-thiophene-azo-naphthalene

$C_{10}H_7.N_2.C_4SH_2.NH_2$. Formed by adding ($\alpha$)-diazo-naphthalene chloride to a solution of thiophenine hydrochloride. The hydrochloride forms microscopic red needles, sparingly soluble in water and alcohol (Stadler, *B.* 18, 2318).

m-Amido-toluene-azo-aceto-acetic acid

[4:2:1] $C_6H_3(CH_3)(NH_2).N_2.CH(CO.CH_3).CO_2H$ [162°]. Red glistening needles. Formed by reduction of *m*-nitro-toluene-azo-aceto-acetic acid with $FeSO_4$ and NH_3 (Bamberger, *B.* 17, 2421).

Amido-toluene-azo-amido-cresol

[4:3:1] $C_6H_3(CH_3)(NH_2).N_2.C_6H_2(CH_3)(NH_2)(OH)$. *Oxyazo-toluidine* [212°]. Small dark-red needles. V. sol. alcohol and ether, sl. sol. water. Formed from amido-toluene-azoxy-toluidine $C_6H_3Me(NH_2).N_2O.C_6H_3Me(NH_2)$ by intramolecular change by heating it with H_2SO_4 at 110°. It is reduced by $SnCl_2$ to tolylene-diamine $C_6H_3Me(NH_2)_2$ [1:2:4] together with di-amido-cresol (Limpricht, *B.* 18, 1405).—$B''H_2SO_4$.—$B''2HCl$.—$B''H_2PtCl_6$.

Amido-toluene-azo-(β)-naphthol

[6:3:1] $C_6H_3(CH_3)(NH_2)—N_2—C_{10}H_6OH$ [1:2].

Acetyl derivative

$C_6H_3(CH_3)(NHAc)—N_2—C_{10}H_6OH$ [276°]. Insol. water, sl. sol. alcohol, m. sol. a mixture of alcohol and chloroform. Red colour. Formed by diazotising the mono-acetyl derivative of (1:2:4)-tolylene-diamine and combining it with (β)-naphthol (Wallach, *B.* 15, 2830).

Amido-toluene-azo-nitro-ethane.

Acetyl derivative $C_{11}H_{14}N_4O_3$ *i.e.* [6:3:1] $C_6H_3Me(NHAc).N_2.CH(NO_2).CH_3$. [143°]. From $C_6H_3Me(NHAc).N_2Br$ and $NaCH(NO_2)CH_3$ (Wallach, *A.* 235, 250). Red needles (from alcohol-ether); v. sl. sol. water, insol. ligroïn.

Amido-toluene-azo-o-toluidine

[4:3:1] $C_6H_3Me(NH_2)—N_2—C_6H_3Me(NH_2)$ [1:4:3] [197°]. Formed by reducing nitro-*o*-toluidine $C_6H_3Me(NO_2)(NH_2)$ [1:4:2], or the corresponding azoxy-compound, by sodium amalgam in alcoholic solution (Limpricht, *B.* 18, 1406; Graeff, *A.* 229, 350). Long red needles (from alcohol) or small yellow needles (from water). Sparingly soluble in water, easily in alcohol and ether.

Salts.—$B''H_2SO_4$: Slender reddish needles —$B''2HCl$.—$(B''2HCl)PtCl_4$.—$B''2HBr$.

Amido-toluene-azo-p-toluidine

[6:3:1] $C_6H_3Me(NH_2)—N_2—C_6H_3Me(NH_2)$ [1:6:3]. [159°]. Red needles. Sl. sol. cold, v. sol. hot, water; v. sol. alcohol. Prepared together with the hydrazo- compound by the prolonged action of sodium amalgam on an alcoholic solution of nitro-*p*-toluidine (Buckney, *B.* 11, 1453).

Di-amyl-amido-benzene-azo-di-amyl-aniline

[4:1] $(C_5H_{11})_2N.C_6H_4—N_2—C_6H_4.N(C_5H_{11})_2$ [1:4]. *Di-amyl-aniline-azyline.* [115°]. Red pointed crystals. Sol. hot alcohol. Formed by passing NO through an alcoholic solution of di-amyl-aniline. Salts.—$B''(C_6H_2(NO_2)_3OH)_2$: small yellow crystals. Periodide B''_4I_6: small black crystals with violet reflex (Lippmann a. Fleissner, *B.* 15, 2142 and *B.* 16, 1419).

Benzene-azo-aceto-acetic acid

$C_6H_5—N_2—CHAc.CO_2H$. [155°]. Yellow leaflets (from alcohol). Prepared by the action of a solution of diazobenzene nitrate on an alkaline solution of acetacetic ether (V. Meyer, *B.* 10, 2076).

Salts.—A'K: yellow glistening leaflets.—BaA'_2, PbA'_2, CuA'_2, and AgA' are yellow pps.

Ethyl ether [75°]. Light yellow crystals; very readily saponified (Züblin, *B.* 11, 1417).

Benzene-azo-acetone $C_6H_5.N_2.CH_2.CO.CH_3$ [149°]. Glistening yellow prisms or needles. Peculiar characteristic smell. Only slightly soluble in hot water, and in aqueous alkalis.

Formation.—1. By heating benzene-azo-aceto-acetic ether with a dilute alcoholic solution of NaOH.—2. By heating benzene-azo-aceto-acetic acid to 170°-180°, CO_2 being evolved (Richter a. Münzer, *B.* 17, 1928).

Benzene-azo-acetophenone

$C_6H_5.N_2.CH_2.CO.C_6H_5$. [129°]. Slender golden needles. V. sol. hot alcohol and hot acetic acid. Formed, together with benzene-azo-benzoyl-acetic ether, by adding a solution of diazo-

benzene chloride to an iced alkaline solution of benzoyl-acetic ether (Bamberger a. Calman, *B.* 18, 2563).

Benzene-o-azo-aniline (?).

$C_6H_5-N_2-C_6H_4NH_2$ (?). [123°]. Formed by reducing benzene-o-azo-nitro-benzene with ammonium sulphide (Janovsky, *M.* 8, 61; yellow crystals with blue reflex (from dilute alcohol). The salts are less soluble in water than those of the *p*-compound.

Benzene-azo-aniline $C_{12}H_{11}N_3$ *i.e.*

$C_6H_5-N_2-C_6H_4NH_2$ [1:4]. *Amido-azo-benzene.* Mol. w. 197. [126°]. (above 360°).

Formation.—1. By reducing benzene-azo-nitro-benzene [137°] with ammonium sulphide (G. Schmidt, *Z.* 5, 417; Janovsky a. Erb, *B.* 18, 1136).—2. Together with bromo-aniline by the action of bromine vapour upon aniline (Kekulé, *Z.* [2] 1, 688).—3. By action of mineral acid (one molecule or less) upon diazo-benzene anilide (*v.* DI-AZO- COMPOUNDS) (Martius a. Griess, *Z.* [2] 1, 132; Friswell a. Green, *C. J.* 49, 746).

Preparation.—1. Diazo-benzene-anilide is dissolved in 2 or 3 times its weight of aniline, $\frac{1}{10}$th its weight of aniline hydrochloride is added at the ordinary temperature, and the mixture is kept for an hour at 30° to 40°; after standing for twenty-four hours at the ordinary temperature, sufficient HCl is added to combine with the free aniline and the amidoazo-benzene base precipitates, or it can be obtained as hydrochloride by adding more HCl. The yield is nearly theoretical (Witt a. Thomas, *C. J.* 43, 113; Staedel a. Bauer, *B.* 19, 1953).—2. A conc. solution (of rather less than 1 mol.) of $NaNO_2$ is added to (1 mol. of) aniline hydrochloride dissolved in (5 or 6 mols. of) aniline at 30°–40°, kept at c. 40° for 1 or 2 hours, and then at the ordinary temperature for 12 hours; completed as above, the yield is nearly theoretical.

Properties.—Yellow crystals; separates from benzene with benzene of crystallisation (W. a. T.); orange prisms with blue reflex (from alcohol). V. sl. sol. hot water, m. sol. ether and alcohol. Its salts are decomposed by water; they dye wool yellow. Tin and HCl give aniline and *p*-phenylene-diamine. Combines with EtI forming the hydriodide of $C_6H_4(NH_2).N_2.C_6H_4NHEt$. The diazo-compounds of benzene-azo-aniline and its sulphonic acids are used for the preparation of scarlets by combination with the naphthols and their sulphonic acids.

Salts.—B'HCl: steel-blue needles or scales (from boiling HClAq).—$B'_2H_2PtCl_6$.—$B'HNO_3$.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Acetyl derivative $C_6H_5.N_2.C_6H_4(NHAc)$. [142°]. Yellow silky crystals. On reduction with alcoholic ammonium sulphide it gives acetyl-amido-hydrazobenzene (Schultz, *B.* 17, 463; Berju, *B.* 17, 1400; *C. C.* 1884, 871).

Reactions.—1. By boiling benzene-azo-aniline with 10 pts. of HCl (S.G. 1·12) it is completely decomposed in a few hours with formation of *p*-phenylene-diamine, aniline, chlorinated-hydroquinones, NH_3, and colouring matters (Wallach a. Kölliker, *B.* 17, 395).—2. An alcoholic solution of bromine forms a dibromo-derivative [152°] which is reduced by tin and HCl to aniline and *p*-phenylene-diamine (Berju, *B.* 17, 1400).—3. With phenyl thio-carbimide it forms benzene-azo-di-phenyl-thio-urea (*q. v.*), together with some benzene-azo-di-phenyl-thio-urea-azo-benzene (*v.* DIS-AZO compounds).—4. Carbonyl chloride forms benzene-azo-di-phenyl-urea-azo-benzene $(Ph-N_2-C_6H_4.NH)_2CO$ (Berju, *B.* 17, 1404).—5. Benzene-azo-aniline hydrochloride (2 mols.) heated with acetone (1 mol.) at 150°–160° under pressure forms a base $C_{17}H_{15}N_3$, [205°]. Yellow needles; v. sol. alcohol, ether, and acids. By tin and HCl it is reduced to a base of melting-point [185°]. Dilute solutions of the salts have a blue fluorescence. Salts.—$B'H_2SO_4$: slender soluble needles or small mono clinic prisms.—$B'H_2Cr_2O_7$: orange-yellow needles. —$B'H_2Cl_2PtCl_4$: flat yellow needles, sl. sol. cold water (Engler a. Schestopal, *B.* 20, 480).

Benzene-azo-benzene $C_{12}H_{10}N_2$ *i.e.*

$C_6H_5-N_2-C_6H_5$. *Azobenzene.* Mol. w. 182. [68°]. (293°). V.D. 6·5 (calc. 6·3). S. (alcohol) 8·5 at 16° (Moltchanoffsky, *J. R.* 1882, 224). S.V. 220·4 (Ramsay).

Formation.—1. By treating nitro-benzene with alcoholic potash (Mitscherlich, *A.* 12, 311; Schmidt a. Schultz, *A.* 207, 328), sodium-amalgam in presence of alcohol and acetic acid (Werigo, *A.* 135, 176; Alexejeff, *Z.* [2] 3, 33), iron (3 pts.) and acetic acid (1 pt.) (Noble, *A.* 98, 253), or with zinc-dust (Alexejeff, *Bl.* [2] 34, 684).—2. By oxidising aniline with aqueous $KMnO_4$ (Glaser, *A.* 142, 364), red-hot PbO (Schichuzky, *J. R.* 6, 245), H_2O_2 (Leeds, *C. N.* 44, 210; *B.* 14, 1382) or bleaching powder (Schmitt, *J. pr.* [2] 18, 195).—3. It is the chief product of the action of sodium on *p*-bromo-aniline (Anschütz a. Schultz, *B.* 9, 1398; *cf.* Claus, *B.* 15, 315).

Preparation.—1. By heating nitro-benzene with a solution of sodium stannite prepared by dissolving the theoretical quantity of $SnCl_2$ in an excess of aqueous NaOH (Witt, *B.* 18, 2912).—2. 400 grms. of NaOH (98 p.c. powdered) are boiled with 2000 c.c. of ordinary alcohol till most has dissolved; 500 g. of nitrobenzene are slowly added to the boiling solution, and the formation of azoxybenzene completed by 2 or 3 hours' cohobation. 200 grms. of zinc-dust are then slowly added and the boiling continued for a day with occasional shaking. The alcohol is distilled off on a salt bath, warm water added, the insoluble portion filtered off, washed, freed from $Zn(OH)_2$ by HCl, and extracted with alcohol; the filtrate on cooling deposits the azobenzene in splendid large plates; good yield.

Properties. — Trimetric plates (Jeremejeff). Crystallises with C_6H_6 from benzene. Its absorption-spectrum has been described by Hartley (*C. J.* 51, 176).

Reactions.—1. Passed through a *red-hot tube* it yields benzene and diphenyl (Ferko, *B.* 20, 664). 2. *Chromic acid* in acetic acid at 200° forms benzene-azoxy-benzene.—3. *Nitric acid* forms $Ph.N_2.C_6H_4(NO_2)$ [1:4], $Ph.N_2.C_6H_4(NO_2)$ [1:2], [4:1] $C_6H_4(NO_2).N_2.C_6H_4(NO_2)$ [1:4], [1:3] $C_6H_4(NO_2).N_2.C_6H_4(NO_2)$ [1:3], and a nitro-benzene-azo-di-nitro-benzene. — 4. Alcoholic *ammonium sulphide* reduces it to hydrazobenzene (Hofmann, *Pr.* 12, 576).—5. Hot conc. HCl, HBr, or HI reduces it to benzidine, other products being formed at the same time.—6. Alcoholic SO_2 produces benzidine.—7. With an ethereal solution of *zinc ethyl* it reacts forming ethane (1 vol.), ethylene (3 vols.), and a

product which, when treated with water, gives aniline. 80 g. of azo-benzene gives 70 g. of aniline. The reactions are probably:—

(a) $PhN_2Ph + 2ZnEt_2 = 2NPhH(ZnEt) + 2C_2H_4$
(b) $PhN_2Ph + 4ZnEt_2 =$
$2NPh(ZnEt)_2 + 2C_2H_6 + 2C_2H_4$.

And then, on adding water:

(a′) $NPhH(ZnEt) + H_2O = NPhH_2 + EtH + ZnO$
(b′) $NPh(ZnEt)_2 + 2H_2O = NPhH_2 + 2EtH + 2ZnO$
(Frankland a. Louis, *C. J.* 37, 560).—8. *Aldehyde* at 200° forms a compound $C_{26}H_{22}N_2O_2$ [164°]. In presence of chloride of zinc, aldehyde condenses with it to benzylidene-benzidine $Ph.CH:N.C_6H_4.C_6H_4.N:CH.Ph$ (?) [239°] (Barzilovsky, *J. R.* 1885, 366).—9. *Bromine* forms mono-bromo- derivatives, a di-bromo- derivative, [205°] (*v.* BROMO-BENZENE-AZO-BROMO-BENZENE), and a tetra-bromo- derivative, $C_{12}H_6Br_4N_2$, [c. 320°] (Werigo, *A.* 165, 200).

Combinations. — $C_{12}H_{10}N_2, C_6H_6$ [38°]. — $(C_{12}H_{10}N_2)_2 3HCl$: unstable yellow crystals. — $(C_{12}H_{10}N_2)_2 3HBr$: unstable red crystals, got by passing HBr into a solution of azobenzene in CS_2.— $C_{12}H_{10}N_2HBr_3$: crystals, formed by adding bromine to a solution of the preceding body in chloroform.—$C_{12}H_{10}N_2Br_6$: red prisms, got by adding excess of bromine to a solution of benzene-azo-benzene in chloroform (Werigo, *A.* 165, 203).

Benzene-azo-benzene sulphonic acid
$C_6H_5—N_2—C_6H_4SO_3H$ [1:4]. [127°]. From benzene-azo-benzene and fuming H_2SO_4 (5 pts.) at 130° (Griess, *A.* 131, 89; 154, 208; Janovsky, *M.* 2, 221; 3, 237; *B.* 15, 2576). Orange-red plates (containing 3aq). Sl. sol. alcohol and ether. Potash-fusion converts it into K_2SO_3 and benzene-azo-phenol. Ammonium sulphide followed by mineral acid converts it into di-amido-di-phenyl sulphonic acid. Nitric acid forms mono-, di-, and tri- nitro- derivatives (Janovsky, *M.* 3, 508).

Salts.—$KA'2aq.$—BaA'_2.—AgA'.

Chloride $C_{12}H_9N_2SO_2Cl$. [82°]. Orange clumps (from ether).

Amide $C_{12}H_9N_2SO_2NH_2$. Powder (Skandaroff, *Z.* [2] 6, 643).

Benzene-azo-benzene disulphonic acid
$C_6H_5—N_2—C_6H_3(SO_3H)_2$ [1:2:4]. Formed, together with *s-m-*, and *s-p-*, sulpho-benzene-azo-benzene sulphonic acids by heating benzene-azo-benzene (1 pt.) with pyrosulphuric acid (4 pts.) at 150° (Janovsky, *M.* 3, 237). Very deliquescent needles. Isomerides of this acid are described as sulpho-benzene-azo-benzene sulphonic acid.

Benzene-azo-benzoic acid
$C_6H_5.N_2.C_6H_4(CO_2H)$ [1:4]. *Azo-benzene-p-carboxylic acid.* Obtained by saponification of its nitrile by boiling with KOH. Long glistening brown prisms. Sol. alcohol, ether, and warm benzene. Salts.—A′K: very soluble brownish-yellow needles.—A'_2Ba: brownish-yellow needles; sol. alcohol, sl. sol. water (Mentha a. Heumann, *B.* 19, 3023).

Nitrile $C_6H_5.N_2.C_6H_4(CN)$ [1:4]. *p-Cyano-azo-benzene.* [101°]. Formed by diazotising benzene-azo-aniline and allowing the solution of diazo-benzene-azo-benzene chloride to drop into a hot solution of $CuSO_4$ and KCN. Brown needles. V. sol. ether, benzene, and warm alcohol, insol. water. Sublimable (M. a. H.).

Benzene-azo-benzoyl-acetic acid
$C_6H_5.N_2.CH(CO.C_6H_5).CO_2H$. [141°]. **Long yellow needles. V. sol. alcohol, ether, and acetic acid.** Its ethyl-ether is formed, together with benzene-azo-acetophenone, by adding a solution of diazobenzene chloride to an iced alkaline solution of benzoyl-acetic ether. By boiling with dilute NaOH it is converted into benzene-azo-acetophenone $C_6H_5.N_2.CH_2.CO.C_6H_5$ (Bamberger a. Calman, *B.* 18, 2563).

Benzene-azo-benzylidene-aniline
$C_6H_5—N_2—C_6H_4.N:CH.C_6H_5$. *Benzylidene-amido-azo-benzene.* [125°]. Orange plates. Formed by the action of benzaldehyde on benzene-azo-aniline. By HCl it is resolved into its constituents (Berju, *B.* 17, 1403).

Benzene-azo-*o*-bromo-benzene
$C_6H_5—N_2—C_6H_4Br$ [1:2]. *Bromo-azo-benzene.* [87°]. Glistening plates (from alcohol). Sl. sol. cold alcohol. By the action of bromine (1 mol.) upon a warm acetic acid solution of benzene-azo-benzene (1 mol.) a mixture of *o*, *m*, and *p*, mono-bromo-benzene-azo-benzene is obtained; they can be separated by their different solubilities in alcohol. By complete reduction they give aniline and *o*-, *m*-, or *p*-bromaniline.

Benzene-azo-*m*-bromo-benzene
$C_6H_5.N_2.C_6H_4Br$ [1:3]. [56°]. Yellowish-green pearly plates. V. sol. alcohol, ether and acetone. On nitration it gives orange needles of $C_{12}H_8Br(NO_2)N_2$ [123°] (Janovsky a. Erb, *B.* 20, 359).

Benzene-azo-*p*-bromo-benzene
$C_6H_5.N_2.C_6H_4Br$ [1:4]. [82°]. Is the chief product of the bromination of benzene-azo-benzene in acetic acid. Orange yellow plat... with limable. V. sol. alcohol, ether... ...tion The corresponding hydr... ...on of white needles. On ... needles of $C_{12}H$... ...aniline di-nitro- derivati... ...$)_2$ [1:4] 19, 2155; 20, 3... ...red pointed BENZENE-AZO-BROM... ...ed by passing

Benzene-azo-t... ...ion of di-amyl $Ph—N_2—C_6Br_3(O$... ...]. ...$)_3OH)_2$: small azo-resorcin and b... ...e (Typke, ...I_6: small blac...

Benzene-azo-*p*-chloro-benzene ...ann a. Fleissner
$C_6H_5—N_2—C_6H_4Cl$ [1:4]. *Ch*... [89°]. Yellowish-brown plateid ...mes in brown needles. Easily soluble in ether, benzene, and hot alcohol, sparingly in cold alcohol.

Preparation.—100 grms. of benzene-azo-aniline hydrochloride are suspended in 2 litres of water and 220 c.c. of conc. HCl, and diazotised by slow addition of a conc. solution of 20 grms. sodium nitrite. After standing for some time the diazo-azo-benzene solution is filtered and slowly added to a boiling solution of 40 grms. Cu_2Cl_2 in 360 c.c. of conc. HCl, and boiled for some time; the greyish-black pp. is treated with conc. HCl and then with dilute NaOH to remove impurities, and extracted with hot alcohol; the alcoholic solution after treatment with animal charcoal deposits the benzene-azo-chloro-benzene on cooling in glistening brown plates; the yield is 38 p.c. of the theoretical (Heumann a. Mentha, *B.* 19, 1686).

Reactions.—When its alcoholic solution is allowed to stand in the cold with $SnCl_2$ and 2 drops of H_2SO_4 it is converted into a chloro-di-amido-diphenyl $NH_2.C_6H_4.C_6H_3Cl.NH_2$. **The**

latter body is not formed, however, by heating the hydrazo- compound, previously prepared, with HCl, but benzene-azo-chloro-benzene, chloro-aniline, and aniline are formed instead. On nitration with fuming HNO_3 benzene-azo-chloro-benzene gives *p*-chloro-benzene-azo-*p*-nitro-benzene $C_6H_4Cl.N_2.C_6H_4(NO_2)$. By treatment with fuming sulphuric acid it is converted into *p*-chloro-benzene-azo-benzene *p*-sulphonic acid $C_6H_4Cl.N_2.C_6H_4(SO_3H)$ (Mentha a. Heumann, *B.* 19, 2970).

Benzene-azo-*o*-cresol

$C_6H_5—N_2—C_6H_3(CH_3)(OH)$ [1:3:4]. [130°]. Glistening yellow plates. V. sol. alcohol, ether, chloroform, and benzene; sl. sol. hot, insol. cold, water. Dissolves in dilute alkalis with a yellowish red colour. Obtained by the action of diazobenzene chloride on an alkaline solution of *o*-cresol. It readily gives a dis-azo- compound when treated in alkaline solution with a further quantity of diazobenzene chloride.

Acetyl derivative: [82°]; yellow tables, v. sol. alcohol, ether, and benzene.

Benzoyl derivative: [111°]; small yellow needles, v. sol. ether, acetone, and hot alcohol (Liebermann a. Kostanecki, *B.* 17, 130; Nölting a. Kohn, *B.* 17, 363).

Benzene-azo-*m*-cresol

$C_6H_5—N_2—C_6H_3(CH_3)(OH)$ [1:2:4]. [109°]. Yellow needles. V. sol. alcohol, ether, chloroform and benzene. With alkalis it forms yellowish-red salts. Obtained by the action of diazobenzene chloride on an alkaline solution of *m*-cresol. It readily combines with another mol. of a diazo- compound to form dis-azo- compounds (Nölting a. Kohn, *B.* 17, 366).

Benzene-azo-*p*-cresol

$C_6H_5—N_2—C_6H_3(CH_3)(OH)$ [1:5:2]. [109°]. Orange yellow plates. Soluble in dilute alkalis. Dyes a canary yellow. Formed by the action of diazo-benzene chloride on an alkaline solution of *p*-cresol. It does not yield a dis-azo- compound.

Acetyl derivative $Ph—N_2—C_7H_6(OAc)$: [68°]; yellow needles, v. sol. alcohol, ether, chloroform, and acetone.

Benzoyl derivative $Ph—N_2—C_7H_6(OBz)$: [113°]; yellow needles, sol. ether, benzene, and hot alcohol (Mazzara, *G.* 9, 425; Liebermann a. Kostanecki, *B.* 17, 130; Nölting a. Kohn, *B.* 17, 352).

Benzene-azo-*p*-cresol-sulphonic acid

$C_6H_5—N_2—C_6H_2(CH_3)(OH)(SO_3H)$ [1:5:2:3]. Small reddish brown tables or needles. Easily soluble in water, sparingly in alcohol. Formed by the action of diazobenzene chloride on an alkaline solution of *p*-cresol-sulphonic acid [1:4:2]. A'Na: soluble reddish brown plates, dyes wool an orange yellow (Nölting a. Kohn, *B.* 17, 357; *cf.* Stebbins, *A. C. J.* 1, 465; 2, 263).

Benzene-azo-ψ-cumenol

$C_6H_5—N_2—C_6H(CH_3)_3OH$ [1:3:5:6:2] [94°]. Glistening brown prisms. In small quantities it can be distilled undecomposed. Insoluble in alkalis. Formed by combining diazo-benzene chloride with ψ-cumenol [70°]. On reduction it yields aniline and amido-ψ-cumenol [167°] (Liebermann a. Kostanecki, *B.* 17, 886).

Benzene-azo-di-ethyl-amido-benzoic acid

$C_6H_5—N_2—C_6H_3(NEt_2)CO_2H$[1:4:2]. [125°]. From diazo-benzene nitrate and di-ethyl-*m*-amido-benzoic acid. Red crystals with violet lustre (from alcohol). Insol. water, sl. sol. alcohol and ether. **Salts**: BaA'_2.—AgA' (Griess, *B.* 10, 526).

Benzene-azo-ethyl-(β)-naphthyl-amine

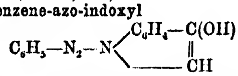
$C_6H_5—N_2—C_{10}H_6.NHEt$. [103°]. Red needles. Soluble in alcohol &c. with an orange-red colour, insol. water. It forms bluish-violet salts with acids. Formed by heating ethyl-(β)-naphthyl-nitrosamine with an acetic acid solution of aniline at 100°. Also produced by combining diazo-benzene with ethyl-(β)-naphthylamine.

Nitrosamine $C_6H_5.N_2.C_{10}H_6.NEt(NO)$: [97°]; red crystals (Henriques, *B.* 17, 2669).

Benzene-azo-ethyl-phenylene-diamine

$C_6H_5.N_2.C_6H_3(NH_2)NHEt$. *Ethyl - chrysoïdine.* Dyes a redder shade than ordinary chrysoïdine. Formed by combining ethyl-*m*-phenylene-diamine with diazo-benzene.—B''HCl: reddish-brown needles with violet-blue reflection, soluble in water and alcohol with an orange colour.—$B''_2H_2Cl_2PtCl_4$; insoluble red pp. (Nölting a. Stricker, *B.* 19, 547).

Benzene-azo-indoxyl

 (?)

[236°]. Red needles or thick orange prisms. Sol. alcohol and alkalis, v. sl. sol. water. Formed by the action of diazo-benzene chloride on indoxyl (Baeyer, *B.* 16, 2190).

Benzene-azo-methane $C_6H_5—N_2—CH_3$. *Azo-phenyl-methyl.* (c. 150°). Yellow oil of peculiar odour. Very volatile, and readily distils with steam. Formed by oxidation of *s*-phenyl-methyl-hydrazine $C_6H_5.NH.NH.CH_3$ with HgO (Tafel, *B.* 18, 1742).

Benzene-azo-methazonic acid

$Ph—N_2—C_2H_3N_2O_3$. [164°]. From diazo-benzene nitrate and an aqueous solution of sodium methazonate (Kimich, *B.* 10, 141). Orange needles (from alcohol); insol. water.—$Na_2A''2aq$.—BaA'' aq.

Benzene-azo-di-methyl-amido-benzoic acid

$Ph—N_2—C_6H_3(NMe_2)CO_2H$ [1:4:2]. From diazo-benzene nitrate and di-methyl-*m*-amido-benzoic acid (Griess, *B.* 10, 527). Orange nodules.

Benzene-azo-methyl-aniline

$C_6H_5—N_2—C_6H_4.NHMe$. *Methyl-amido-azo-benzene.* [180°]. Red needles. Sol. alcohol. Formed by heating benzene-azo-aniline with MeI.—B'HCl: violet needles.

Acetyl derivative $C_6H_5.N_2.C_6H_4.NMeAc$: [139°]; yellow silky needles (Berju, *B.* 17, 1401).

Benzene-azo-di-methyl-aniline

$C_6H_5.N_2.C_6H_4.NMe_2$. *Dimethyl-amido-azo-benzene.* [115°]. Yellow plates.

Preparation.—1. A solution of 74 pts. of $NaNO_2$ (100 p.c.) and 40 pts. of NaOH in 540 pts. of water is slowly added to a cooled solution of 100 pts. of aniline, 130 pts. of dimethylaniline, and 230 pts. of HCl in 360 pts. of water (Griess, *B.* 10, 525: Möhlau, *B.* 17, 1490).—2. By heating benzene-azo-aniline with MeI (Berju, *B.* 17, 1402; *C. C.* 1884, 871).

Methylo-iodide B'MeI. [174°]. Plates.

Benzene-azo-methyl-ketole

$C_6H_5—N_2—C_9H_8N$. [116°]. Yellow needles. Formed by the action of diazo-benzene-chloride upon methyl-ketole in aqueous alcoholic solution in presence of sodium-acetate (Fischer, *B.* 19, 2990).

Benzene-azo-methyl-phenylene-diamine $C_6H_5.N_2.C_6H_3(NH_2)NHMe$. *Methyl-chrysoïdine.* Minute orange prisms. Dyes a somewhat redder shade than ordinary chrysoïdine. Formed by combining diazobenzene with methyl-*m*-phenylene diamine (Nölting a. Stricker, *B.* 19, 549).

Benzene-azo-(α)-naphthol $C_6H_5-N_2-C_{10}H_6.OH$. (α)-*Naphthoquinone-phenyl-hydrazide.* [206°]. Small needles with blue reflection (from alcohol) or flat needles or plates (from benzene).

Formation.—1. By combining (α)-naphthol with diazobenzene.—2. By the action of phenylhydrazine hydrochloride upon (α)-napthoquinone suspended in acetic acid.

Reactions.—Dissolves both in acids and alkalis. Bromine forms two bromo- derivatives [185°], and [196°] (Margary, *G.* 14, 271).

Salts.—A'K: crystalline pp. The **hydrochloride**, **hydrobromide**, and **sulphate** form bluish or greenish glistening needles, sparingly soluble in water, alcohol, and acetic acid (Typke, *B.* 10, 1580).

Methyl ether A'Me: [83°]; brown crystals.

Ethyl ether A'Et: [100°]; long needles.

Acetyl derivative $C_{16}H_{11}N_2(OAc)$ [128°]; small brownish-red needles (Liebermann, *B.* 16, 2858; Zincke a. Bindewald, *B.* 17, 3026).

Benzene-*o*-azo-(α)-naphthol

$C_{10}H_6\left\langle\begin{array}{l} O\alpha \\ \;| \\ N_2H.C_6H_5\beta \end{array}\right.$ [1:2]. (?) [138°]. (β)-*Naphthoquinone-phenyl-hydrazide.* Formed by the action of phenylhydrazine hydrochloride upon (β)-naphthoquinone. Long red needles; sol. hot alcohol and hot acetic acid. It does not combine with acids or bases. By $SnCl_2$ it is reduced to (β)-amido-(α)-naphthol. By treatment in hot acetic acid solution with HNO_3 it gives di-nitro-(α)-naphthol. By the action of alkaline reducing agents it is at once converted into (β)-amido-(α)-naphthol; no intermediate product could be detected (Zincke a. Bindewald, *B.* 17, 3030; Zincke a. Rathgen, *B.* 19, 2182).

Bromo- derivative $C_{16}H_{10}N_2Br_2O$; [215°-219°]: slender red needles.

Benzene-azo-(β)-naphthol $C_{16}H_{12}N_2O$ *i.e.*

$C_6H_5.N_2.C_{10}H_6.OH$ or $C_{10}H_6\left\langle\begin{array}{l} O\beta \\ \;| \\ N_2H.C_6H_5\alpha \end{array}\right.$ [1:2]. [134°].

Formation.—By the action of a diazobenzene salt on an alkaline solution of β-naphthol. It is *not* formed by the action of diazobenzene hydrate on finely divided (β)-naphthol (difference from (α)-naphthol) (Liebermann, *B.* 16, 2858).

Properties.—Golden plates or long metallic glistening needles. Soluble in ether, benzene, ligroine and CS_2. Dissolves in H_2SO_4 with a magenta-red colour. Is insoluble in caustic alkalis. It has a slightly basic character, dissolving in HCl with a red colour, and forming an unstable hydrochloride crystallising in needles. By $SnCl_2$ it is reduced to (α)-amido-(β)-naphthol and aniline. The same reduction products are also formed at once by treatment with alkaline reducing agents (*e.g.* zinc-dust and NaOH, ammonium sulphide, &c.); no intermediate product was detected. When treated in hot acetic acid solution with HNO_3 it gives di-nitro-(β)-naphthol (Zincke a. Rathgen, *B.* 19, 2482).

Bromo- derivative $C_{16}H_{11}BrN_2O$: [168°]. Brownish-red needles (Zincke a. Bindewald, *B* 17, 3031).

Benzene-azo-(α)-naphthol sulphonic acid $C_6H_5-N_2-C_{10}H_5(SO_3H)(OH)$. From sodium (α)-naphthol sulphonate, aniline nitrate, and KNO_2 (Hofmann, *B.* 10, 1378). Slender brown needles (from alcohol mixed with HClAq). Dyes orange.—AgA'.—BaA'_2.

Benzene-azo-(β)-naphthol sulphonic acid $C_6H_5-N_2-C_{10}H_5(HSO_3)OH$. Brown needles with yellowish-green reflex. Difficultly soluble in water and alcohol. Prepared by the action of an alkaline solution of (β)-naphthol-sulphonic acid on diazobenzene nitrate or chloride.—A'_2Ba. Yellowish red microscopic leaflets. Slightly soluble in water (Griess, *B.* 11, 2197). Its absorption-spectrum has been examined by Hartley (*C. J.* 51, 196).

Benzene-azo (β)-naphthol disulphonic acid $C_6H_5-N_2-C_{10}H_4(SO_3H)_2(OH)$. From sodium (β)-naphthol disulphonate and diazo-benzene nitrate. Sol. water. **Barium salt** is sl. sol. water (Stebbins, jun., *A. C. J.* 2, 236).

Benzene-azo-(α)-naphthylamine $C_6H_5-N_2-C_{10}H_6NH_2$. Prepared by the action of diazobenzene sulphate on (α)-naphthylamine (Griess, *T.* 1864, iii. 679; Weselsky a. Benedikt, *B.* 12, 228).—$B'_2H_2SO_4$4aq: microscopic needles; difficultly soluble in water.

Benzene-azo-(β)-naphthylamine

$C_6H_5-N_2-C_{10}H_6NH_2$ or $C_{10}H_6\left\langle\begin{array}{l} NH \\ \;| \\ N_2H.C_6H_5 \end{array}\right.$.

Benzene-hydrazimido-naphthalene. [104°]. Red trimetric tables or long fine red needles. Easily soluble in alcohol and acetic acid, insoluble in water. Dissolves in strong H_2SO_4 with a blue colour. Its salts exist only in presence of a large excess of acid. Formed by combination of diazobenzene with (β)-naphthylamine. By boiling with 20 p.c. aqueous H_2SO_4 it is slowly decomposed into (β)-naphthylamine, phenol, and nitrogen. On reduction it gives aniline and (1, 2)-naphthylene diamine. On oxidation it gives benzene-azimido-naphthalene (*q.v.*).

Acetyl derivative $C_{16}H_{12}AcN_3$. [153°]. Small red needles, easily soluble in alcohol, insoluble in water.

Benzoyl derivative $C_{16}H_{12}BzN_3$: [163°], red crystals (Lawson, *B.* 18, 796).

Benzene-*o*-azo-nitro-benzene $C_6H_5-N_2-C_6H_4(NO_2)$ [1:2]. *Nitro-azobenzene.* [123°]. Formed by nitration of benzene-azo-benzene in acetic acid at 100°. Orange-yellow minute needles. V. sol. alcohol. Alcoholic NaOH gives a beautiful emerald-green colouration; by long boiling or by treatment with sodium-amalgam it is further reduced to a compound $C_{24}H_{18}N_6O$. Tin and HCl or ammonium sulphide first reduce it to benzene-*o*-azo-aniline and then to aniline, and *o*-phenylene-diamine. By bromination in acetic acid it yields bromo-nitrobenzene [123°] or [132°] (Janovsky a. Erb, *B.* 19, 2157; 20, 360; *M.* 8, 56).

Benzene-*p*-azo-nitro-benzene $C_6H_5.N_2.C_6H_4.NO_2$ [1:4]. [137°]. Small yellow needles (from alcohol). Formed by nitration of benzene-azo-benzene. By NH_4HS it is reduced

to ordinary benzene-azo-aniline. Alcoholic NH_4HS produces red crystals of an intermediate nitrolic acid $\begin{matrix} C_6H_5.N_2.C_6H_4.NOH \\ | \\ C_6H_5.N_2.C_6H_4.NOH \end{matrix}$ (?) [134°], which forms a blue solution in NaOHAq. K_3FeCy_6 reoxidises it to benzene-azo-*p*-nitrobenzene. By complete reduction it yields aniline and *p*-phenylene-diamine (Laurent a. Gerhardt, *A.* 75, 73; Janovsky, *B.* 18, 1133; *M.* 6, 164, 455).

Benzene-azo-tri-nitro-benzene $C_6H_5-N_2-C_6H_2(NO_2)_3$. [112°]. By action of HgO on an alcoholic solution of the corresponding hydrazo- compound (E. Fischer, *A.* 190, 133). Slender red prisms (from alcohol).

Benzene-azo-nitro-iso-butane $C_6H_5-N_2-CH(NO_2)Pr$. From diazobenzene nitrate and potassium nitro-iso-butane (Züblin, *B.* 10, 2088). Oil. Forms an orange solution in alkalis.

Benzene-azo-nitro-ethane $C_8H_9N_3O_2$ *i.e.* $C_6H_5-N_2-CH(NO_2).CH_3$. [137°]. From diazobenzene nitrate and sodium nitroethane (V. Meyer a. Ambühl, *B.* 8, 751, 1073). Rectangular orange crystals; v. sol. alcohol and ether, insol. cold water, sol. aqueous alkalis forming a blood-red solution. Dyes silk yellow. Conc. H_2SO_4 forms a violet solution. It crystallises unaltered from aqueous NH_3 (Barbieri, *B.* 9, 386) but such a solution gives pps. with metallic salts.

S a l t s.—$C_8H_7K_2N_3O_2$4aq.—$C_8H_7Na_2N_3O_2$7aq.—$C_8H_7ZnN_3O_2$3aq.—$C_8H_7PbN_3O_2PbO$ 2½aq.

Benzene-azo-nitro-methane $C_6H_5-N_2-CH_2.NO_2$. [153°]. From diazobenzene nitrate and sodium nitromethane in very dilute solution (Friese, *B.* 8, 1078). Slender red needles (from alcohol). Conc. H_2SO_4 gives a purple solution. Decomposed by HClAq only after long boiling.

Benzene-azo-tri-nitro-phenol $C_6H_5-N_2-C_6H(NO_2)_3OH$. Long brown prisms. Insol. cold, sl. sol. hot, water; v. sol. alcohol. Explodes at 70°. Dyes silk and wool orange-yellow. Prepared by the action of a salt of diazobenzene on an alcoholic solution of picric acid (Stebbins, jun., *A. C. J.* 1, 465; 2, 236; *C. N.* 41, 117; *B.* 13, 43).

Benzene-azo-nitro-propane $C_6H_5-N_2-CH(NO_2).CH_2.CH_3$. [99°]. From potassium nitropropane and diazobenzene nitrate (V. Meyer, *B.* 9, 386). Orange needles; sol. alkalis.

Benzene-azo-iso-nitro-propane $C_6H_5-N_2-C(NO_2)(CH_3)_2$. From aqueous diazobenzene nitrate and potassium nitro-isopropane. Oil; insol. alkalis (V. Meyer a. Ambühl, *B.* 8, 1076).

Benzene-azo-*o*-oxy-benzoic-acid $C_6H_5-N_2-C_6H_3(OH).CO_2H$. From diazobenzene nitrate and an alkaline solution of salicylic acid (Stebbins, jun., *A. C. J.* 1, 465; *B.* 13, 715; *C. N.* 41, 117). Orange-red needles; insol. water, v. sol. alcohol or ether. Dyes wool orange.

Benzene-azo-di-oxy-naphthalene $C_6H_5-N_2-C_{10}H_5(OH)_2$ or $C_{10}H_5(OH)\begin{cases} O \\ N_2HC_6H_5 \end{cases}$. *Oxy-(α)-naphthoquinone phenyl-hydrazide.* [230°]. Formed by the action of phenyl-hydrazine on oxy-naphthoquinone in aqueous-alcoholic solution. Yellowish-red glistening needles. V. sol. ether, hot alcohol, and hot acetic acid.

S a l t s.—The alkali salts form slender orange needles, sol. alcohol.—A'_2Ba 10aq: yellowish-brown plates or long red needles.—A'_2Ca 4aq: slender orange needles.—A'Ag: reddish-brown amorphous pp.

Acetyl derivative: [179°]; red needles.

Methyl ether A'Me: [175°]; red needles.

Ethyl ether A'Et: [173°]; yellowish-red needles, v. sol. hot alcohol and hot acetic acid.

Bromo-derivative $C_{16}H_{11}BrO_2N_2$: [198°]; large red needles, sl. sol. alcohol (Zincke a. Thelen, *B.* 17, 1809).

Benzene-azo-phenol $C_6H_5-N_2-C_6H_4.OH$[1:4]. *Oxy-azo-benzene.* [154°].

Formation.—1. A product of the action of cold $BaCO_3$ on diazobenzene nitrate in the cold (Griess, *A.* 137, 84).—2. From benzene-azo-benzene sulphonic acid by potash fusion (Griess, *A.* 154, 211).—3. From diazo-benzene nitrate and C_6H_5OK (Kekulé a. Heidegh, *Z.* [2] 6, 384).—4. By the action of *p*-nitroso-phenol (20 pts.) on aniline acetate (60 pts.) (Kimich, *B.* 8, 1499).—5. By gently warming benzene-azoxy-benzene, $C_6H_5-N_2O-C_6H_5$, with H_2SO_4 (Wallach, *B.* 13, 525; 14, 2617).

Properties.—Purple pyramidal plates. Insol. cold water, sol. alkalis; v. sol. alcohol. Bromine in acetic acid gives a compound [139°].

S a l t.—AgA'.

Acetyl derivative.—$Ph.N_2.C_6H_4OAc$. [85°]. (above 360°). Golden scales.

Methyl ether.—$Ph.N_2.C_6H_4OMe$ [54°]. Yellow scales.

Benzene-azo-phenol sulphonic acid $C_6H_5-N_2-C_6H_3(OH)(SO_3H)$[1:4:3]. From diazobenzene nitrate and an alkaline solution of phenol *o*-sulphonic acid (Griess, *B.* 11, 2194). Red needles or tables; sol. water and alcohol.—KA'.

Benzene-azo-phenol sulphonic acid $C_{12}H_8N_2(OH)(SO_3H)$. From benzene-azo-phenol and fuming H_2SO_4 (Tschirvinsky, *B.* 6, 560).—$BaA'_2$2aq.—$CuA'_2$6aq.—$MgA'_2$6aq.—KA'.

Benzene-azo-phenol di-sulphonic acid $C_{12}H_7N_2(OH)(SO_3H)_2$. From azoxybenzene (1 pt.) and fuming H_2SO_4 (10 pts.) by heating for 3 hours at 150° (Limpricht a. Wilsing, *A.* 215, 232; *B.* 15, 1297). Orange needles, v. e. sol. water, v. sol. dilute acids.

S a l t s.—K_2A'' 2aq: red needles, sl. sol. cold water; not attacked by Br.—BaA''aq: orange crystalline pp.—Ag_2A'': red crystalline pp.

Benzene-azo-phenol tetra-sulphonic acid $C_{12}H_5N_2(OH)(SO_3H)_4$. From azoxybenzene and fuming H_2SO_4 (L. a. W.). Will not crystallise. S a l t s.—$C_{12}H_5N_2(OK)(SO_3K)_4$7½aq; long yellow needles. Gives with bromine-water a pp. of tri-bromo-phenol [92°].—Ba_2A^{iv} 7aq: orange crystalline pp.

Other benzene-azo-phenol sulphonic acids are described as *Oxy-benzene-*AZO*-benzene sulphonic acids*, and *sulpho-benzene-*AZO*-phenol sulphonic acids.*

Benzene-azo-diphenylamine $C_6H_5-N_2-C_6H_4.NH.C_6H_5$. [82°] (O. N. Witt, *C. J.* 35, 185; *B.* 12, 259). A solution of diphenylamine (17 g.) in alcohol (100 c.c.) is added to a solution of diazo-benzene chloride (14 g.) in alcohol (50 g.). The brown mixture is cooled with ice, and alcoholic NMe_3 (used instead of NH_3 because NMe_3HCl is soluble in alcohol) is

added from time to time to neutralise the liquid. The oil which separates is purified by a lengthy process, and finally crystallised from benzoline.

Properties.—Golden leaflets or needles. Sol. benzene, alcohol, and ether. HCl turns its alcoholic solution violet; steel-grey crystals of the hydrochloride separating. The base forms a green solution with H_2SO_4 turned, by adding water, into indigo, violet, and finally red. With amyl nitrite and acetic acid it forms a nitrosamine, Ph.N(NO).$C_6H_4N_2$Ph, [120°], forming orange needles, sparingly soluble in alcohol and acetic acid, readily in benzene.

Benzene-azo-*m*-phenylene diamine
C_6H_5—N_2—$C_6H_3(NH_2)_2$ [1:2:4]. *Chrysoïdine.* [117·5°] (W.); [110°] (H.). From diazobenzene salts and *m*-phenylene diamine (Witt, *B.* 10, 350, 654; Hofmann, *B.* 10, 213, 388; Griess, *B.* 10, 390). Slender yellow needles (from water); sl. sol. water, v. sol. alcohol. Reduced by ammonium sulphide at 150° to aniline and (1, 2, 4)-tri-amido-benzene. The absorption-spectrum has been examined by Hartley (*C. J.* 51, 178).—B″HCl: black octahedra or small red silky crystals; its aqueous solution is orange, but turned red by HCl—B″$_2H_2PtCl_6$.—B″HNO_3.

Di-acetyl derivative
Ph—N_2—C_6H_3(NHAc)$_2$ [251°].

Benzene-azo-*m*-phenylene-diamine sulphonic acid C_6H_5—N_2—$C_6H_2(NH_2)_2(SO_3H)$. *Chrysoïdine sulphonic acid.* Glistening spangles or needles. Sl. sol. water and alcohol. Prepared by the action of diazobenzene-chloride on a salt of *m*-phenylene-diamine sulphonic acid. A′Na: soluble golden needles—A′$_2$Ba: orange needles (Ruhemann, *B.* 14, 2655). By the sulphonation of chrysoïdine an isomeric acid is formed (*v. Di-amido-benzene-azo-benzene sulphonic acid*).

Benzene-azo-di-phenyl-methyl-pyrrol-carboxylic acid $C_{24}H_{19}O_2N_3$ *i.e.*
$HO_2C.C:CMe$
$\quad\quad | \quad\quad \rangle N.C_6H_4.N_2.C_6H_5$. [195°]. Obtained
$HC:CPh$
by saponification of its ethyl ether, which is formed from an acetic acid solution of aceto-phenone-aceto-acetic ether (1 mol.) and benzene-*p*-azo-aniline (1 mol.) on standing for two days. Large red crystals. V. sol. alcohol, ether, and benzene; sl. sol. ligroïn and acetic acid; insol. water, and conc. acids. Gives Laubenheimer's reaction.

Ethyl ether EtA′: [123°]; splendid red crystals; v. sol. benzene and ligroïn, sl. sol. alcohol, ether, and acetic acid (Paal a. Schneider, *B.* 19, 3162).

Benzene-azo-phenyl-(β)-naphthyl-amine
$C_{22}H_{17}N_3$ *i.e.* C_6H_5—N_2—$C_{10}H_6NHC_6H_5$ or
$C_{10}H_6\langle$ N.C$_6H_5$ | N.HC$_6H_5$ $\rangle$.
Benzene - phenyl - hydrazimido - naphthalene. [142°]. Obtained by combining diazo-benzene chloride with phenyl-(β)-naphthyl-amine in alcoholic solution. It is also formed by the action of an acetic acid solution of aniline upon phenyl-(β)-naphthyl-nitrosamine. Small red glistening needles.

Reactions.—1. By heating with conc. HCl it yields naphthophenazine $C_6H_4\langle$ N | N $\rangle C_{10}H_6$ and aniline.—2. *Bromine* acting on the hot acetic acid solution forms tetra-bromo-phenyl-(β)-naphthylamine with evolution of nitrogen.—3. It is *reduced* by $SnCl_2$ to aniline and phenyl-*o*-naphthylene diamine $C_{10}H_6(NH_2)NHC_6H_5$.—4. By *oxidation* with $K_2Cr_2O_7$ in acetic acid solution the chromate of a powerful ammonium-base $C_{22}H_{16}N_3OH$ is formed; the latter possibly has the constitution $C_{10}H_6\langle$ N(OH).C$_6H_5$ | N.N.C$_6H_5$ $\rangle$ *v. Naphthalene di-phenyl-*AZAMMONIUM-*hydrate* (Henriques, *B.* 17, 2671: Zincke a. Lawson, *B.* 20, 1167).

Benzene-azo-di-phenyl-thio-urea
C_6H_5—N_2—C_6H_4.NH.CS.NHPh. [179°]. Plates. Formed by combination of phenyl-mustard-oil with benzene-azo-aniline (Berju, *B.* 17, 1405).

Benzene-azo-pyrogallol
C_6H_5—N_2—$C_6H_2(OH)_3$. Prepared by adding an aqueous solution of diazobenzene nitrate to an alkaline solution of pyrogallol (Stebbins, jun., *A. C. J.* 1, 465; 2, 236; *B.* 13, 44; *C. N.* 41, 117). Red needles (from acetic acid). Insol. water, sol. alcohol. Its alcoholic solution dyes silk and wool orange.

Benzene-*p*-azo-resorcin
C_6H_5—N_2—$C_6H_3(OH)_2$ [1:2:4]. [161°] or [170°]. From diazobenzene nitrate and resorcin (Typke, *B.* 10, 1577; Wallach, *B.* 15, 2819; R. Meyer, *B.* 16, 1329). Formed also by gently warming diazobenzene anilide with resorcin, aniline being eliminated (Heumann a. Oeconomides, *B.* 20, 905). Slender orange needles [170°] or short red needles [161°], insol. water, sol. aqueous alkalis, v. e. sol. alcohol.

Acetyl derivative [102°].

Mono-ethyl ether [87°]. Scarlet needles.

Diethyl ether [70°]. Yellowish-red needles.

Benzene-*o*-azo-resorcin $C_6H_5.N_2.C_6H_3(OH)_2$ [1:2:6]. Formed in small quantity (about 5 p.c.) in the preparation of the *p*-isomeride.

Mono-ethyl ether $C_6H_5.N_2.C_6H_3$(OH)(OEt) [150°]. Long fine scarlet needles; v. e. sol. alcohol and ether, insol. water; dissolves in aqueous alkalis with a brownish-red colour.

Di-ethyl-ether $C_6H_5.N_2.C_6H_3(OEt)_2$: [90°]. Large red glistening tables; v. sol. ether, hot alcohol and acetic acid, insol. water (Pukall, *B.* 20, 1145).

Benzene-azo-thymol
C_6H_5—N_2—C_6H_2MePr(OH) [1:2:5:4] [85°-90°]. From diazobenzene chloride, and an alkaline solution of thymol (Mazzara, *G.* 15, 52, 228). Reddish-yellow needles. Reduction followed by oxidation gives thymoquinone.

Benzene-azo-thymol-sulphonic acid
C_6H_5—N_2—$C_6H(CH_3)(C_3H_7)(HSO_3)$OH. [216°]. Small yellow prisms. Yellow colouring matter. Prepared by the action of diazobenzene chloride on a salt of thymol-sulphonic acid. Salts.—A′Na: small yellow crystals.—A′$_2$Ba: fine hair-like needles (Stebbins, *B.* 14, 2793).

Benzene-*p*-azo-toluene C_6H_5—N_2—$C_6H_4(CH_3)$ [63° corr.]. Formed by diazotising amido-benzene-*p*-azo-toluene $C_6H_4(CH_3)$—N_2—$C_6H_4(NH_2)$ dissolved in alcohol and boiling the solution (Schultz, *B.* 17, 466). Orange-red plates; v. sol. alcohol. Volatile with steam. **By treatment with alcoholic $SnCl_2$ and H_2SO_4 it is converted into a base melting at [116°].**

Benzene-azo-*m*-tolylene diamine C_6H_5—N_2—$C_6H_2Me(NH_2)_2$. Yellow needles. Easily soluble in alcohol, sparingly in water. Prepared by the action of diazobenzene chloride on (1, 2, 4) tolylene-diamine, [99°].—B'HCl: orange red needles (Stebbins, jun., *A. C. J.* 1, 465; *B.* 13, 717; *C. N.* 41, 117).

Benzene-azo-xylenol $C_6H_5.N_2.C_6H_2Me_2.OH$ [1:3:5:2]. [175°]. Formed by combining diazobenzene chloride with *m*-xylenol $C_6H_3Me_2(OH)$ [1:3:4] (Grevingk, *B.* 19, 148). Slender brownish-red needles. V. sol. alcohol, ether, and benzene, insol. water. On reduction it yields aniline and *o*-amido-*m*-xylenol $C_6H_2Me_2(NH_2)(OH)$ [5:3:2:1].

Bromo-amido-benzene-azo-*p*-bromo-aniline *Diacetyl derivative* [2:5:1] $NHAc.C_6H_3Br$—N_2—$C_6H_3Br.NHAc$[1:5:2] [282°]. Formed by warming acetyl-bromo-nitro-aniline $C_6H_3(NHAc)Br(NO_2)$ [2:5:1] with zinc and conc. NH_3Aq (C. H. Matthiessen a. Mixter, *Am.* 8, 347). Pale red substance.

***p*-Bromo-benzene-azo-benzene-*p*-sulphonic acid** [4:1] C_6H_4Br — N_2 — $C_6H_4(SO_3H)$ [1:4]. Formed by sulphonation of benzene-*p*-azo-bromo-benzene or by bromination of benzene-azo-benzene-*p*-sulphonic acid. Flat needles (containing 3aq).

Salts. — KA': rhombic tables. — NaA': yellow silky needles, sl. sol. water (Janovsky, *M.* 5, 162; *B.* 20, 358; *M.* 8, 53).

***m*-Bromo-benzene-azo-benzene-*p*-sulphonic acid** [3:1] C_6H_4Br—N_2—$C_6H_4(SO_3H)$ [1:4]. Formed by sulphonation of benzene-*m*-azo-bromo-benzene with fuming sulphuric acid. Glistening golden plates (containing $1\frac{1}{2}$ aq).

Salts.—KA': yellow pearly pp. of microscopic needles.—NaA': pp. v. sl. sol. water (Janovsky a. Erb, *B.* 20, 359).

***o*-Bromo-benzene-*o*-azo-bromo-benzene** [2:1] C_6H_4Br—N_2—C_6H_4Br [1:2]. [185°]. A product of the bromination of benzene-azo-benzene in HOAc (Janovsky, *M.* 8, 50; *B.* 20, 337). Golden plates, sl. sol. alcohol. On nitration it gives a tri-nitro- derivative [135°].

***p*-Bromo-benzene-*p*-azo-bromo-benzene** [4:1] C_6H_4Br—N_2—C_6H_4Br [1:4]. [205°]. Formed by bromination of benzene-azo-benzene (Werigo, *A.* 135, 178; 165, 189). Formed also by reduction of *p*-bromo-nitro-benzene with zinc-dust and alcoholic KOH (Schultz, *B.* 17, 465). Yellow needles. By alcoholic $SnCl_2$ and H_2SO_4 it is converted into a di-bromo-di-amido-diphenyl. Fuming H_2SO_4 forms a sulphonic acid $C_{12}H_7Br_2N_2SO_3H$ 3aq (W.).

***m*-Bromo-benzene-*m*-azo-bromo-benzene** [3:1] C_6H_4Br—N_2—C_6H_4Br [1:3]. [126°]. From the corresponding hydrazo- compound by Fe_2Cl_6 (Gabriel, *B.* 9, 1407).

Tribromo-benzene-azo-dimethyl-aniline $C_6H_2Br_3$—N_2—$C_6H_4(NMe_2)$. [161°]. Formed by adding an alcoholic solution of dimethylaniline (2 mol.) to $C_6H_2Br_3N_2.NO_3$ (1 mol.). Crystalline pp. Red plates (from glacial acetic acid). Insol. water, hardly soluble in alcohol. It combines with conc. HCl (Silberstein, *J. pr.* [2] 27, 124).

Tribromo-benzene-azo-methyl-diphenylamine $C_6H_2Br_3$—N_2—C_6H_4NPhMe. [138°]. From $C_6H_2Br_3N_2NO_3$ and NPh_2Me in alcohol. Small brownish-red plates (from glacial acetic acid). Insol. water, sl. sol. alcohol. Does not combine with HCl (Silberstein, *J. pr.* [2] 27, 125).

Bromo-benzene-azo-(α)-naphthol [4:1] C_6H_4Br—N_2—$C_{10}H_6OH$ [1:4]. [196°]. From *p*-diazo-bromo-benzene and (α)-naphthol, or by bromination of benzene-azo-(α)-naphthol (Mazzara, *G.* 14, 271).

***p*-Bromo-benzene-azo-(β)-naphthol** [4:1] C_6H_4Br—N_2—$C_{10}H_6OH$ [1:2]. [161°]. From *p*-diazo-bromo-benzene and (β)-naphthol, or from benzene-azo-(β)-naphthol and bromine (Mazzara, *G.* 13, 438). Orange needles.

***p*-Bromo-benzene-*p*-azo-nitro-benzene** [4:1] C_6H_4Br—N_2—$C_6H_4(NO_2)$ [1:4]. [108°]. Formed by nitration of benzene-*p*-azo-bromo-benzene. Yellow needles. V. sol. alcohol (Janovsky a. Erb, *B.* 20, 358).

Bromo-benzene-azo-di-nitro-benzene (?) [4:1] C_6H_4Br—N_2—$C_6H_3(NO_2)_2$ [1:2:4] (?). [190°]. Formed by nitrating benzene-*p*-azo-bromo-benzene (Janovsky, *M.* 8, 52).

***p*-Bromo-benzene-azo-nitro-ethane** [4:1] C_6H_4Br—N_2—$CH(NO_2).CH_3$. [c. 137°]. From *p*-diazo-bromo-benzene nitrate and potassium nitro-ethane (Wald, *B.* 9, 393). Brick-red crystals (from dilute alcohol); sol. ether, glacial HOAc, and chloroform. Salt.—$C_8H_7KN_3O_2Br$.

Di-bromo-di-imido-di-hydro-anthracene-azo-di-bromo-di-imido-di-hydro-anthracene $C_{14}H_7Br_2N_3$ or

$$C_6H_4\!\left\langle\begin{matrix}\overset{\displaystyle NH}{C}\\ \underset{\displaystyle NH}{C}\end{matrix}\right\rangle\!C_6Br_2H—N_2—Br_2HC_6\!\left\langle\begin{matrix}\overset{\displaystyle NH}{C}\\ \underset{\displaystyle NH}{C}\end{matrix}\right\rangle\!C_6H_4\ (?)$$

[233°]. Prepared by heating dibromo-nitro-anthraquinone with alcoholic NH_3 (Claus a. Diernfellner, *B.* 14, 1335). Red needles. Sublimable. Sl. sol. alcohol and ether, insol. water or aqueous acids and alkalis.

Bromo-di-oxy-benzene-azo-bromo-hydroquinone. *Tetra-methyl derivative* $C_6H_2Br(OMe)_2$—N_2—$C_6H_2Br(OMe)_2$. [220°]. Formed by bromination of the tetra-methyl derivative of di-oxy-benzene-azo-hydroquinone (Baessler, *B.* 17, 2125). Red crystalline solid, v. sol. benzene, chloroform, and CS_2, v. sl. sol. alcohol, insol. water.

Bromo-sulpho-benzene-azo-benzene sulphonic acid [6:3:1]$C_6H_3Br(SO_3H)$—N_2—$C_6H_3Br[SO_3H)$[1:6:3]. Formed by oxidation of a neutral aqueous solution of bromo-amido-benzene sulphonic acid $C_6H_3Br(NH_2)(SO_3H)$ [4:3:1] with $KMnO_4$. Salts.—K_2A''2aq: glistening red tables (Limpricht, *B.* 18, 1422).

Di-bromo-sulpho-benzene-azo-di-bromo-benzene sulphonic acid [2:6:4:1]$C_6H_2Br_2(SO_3H).N_2.C_6H_2Br_2SO_3H$[1:2:6:4]. From potassic di-bromo-*o*-amido-benzene sulphonate and $KMnO_4$ (Rodatz, *A.* 215, 222). Red plates (containing 2aq). V. sol. water or alcohol. Reduced by $SnCl_2$ to the original $C_6H_2(NH_2)Br_2SO_3H$. Salts. — K_2A''2aq. — BaA''3aq.—CaA''4aq.—PbA''.

Chloride.—[258°–262°]. Brown plates.

Amide.—Violet silky needles.

Di-bromo-sulpho-benzene-azo-di-bromo-benzene sulphonic acid [4:6:3:1]$C_6H_2Br_2(SO_3H).N_2.C_6H_2Br_2SO_3H$[1:4:6:3]. From potassic di-bromo-amido-benzene sulphonate and $KMnO_4$ (Rodatz, *A.* 215, 216). Slender red needles, containing $1\frac{1}{2}$ aq (from water). V. sol. water, v. e. sol. alcohol. Reduced by $SnCl_2$

to the original $C_6H_2(NH_2)Br_2.SO_3H$. **Salts.**—$K_2A''3aq.$—$BaA''aq.$—$CaA''4aq.$—$PbA''2\frac{1}{2}aq.$

Chloride.—[233°]. Brick-red needles.

Amide.—Microscopic orange needles (from alcohol). Does not melt.

An acid isomeric with the above may be got by the action of $KMnO_4$ on the tetra-bromo-hydrazo-benzene di-sulphonic acid of Jordan, *A.* 202, 361.

Tri-bromo-sulpho-benzene-azo-tri-bromo-benzene sulphonic acid [2:4:6:3:1] $C_6HBr_3(SO_3H)-N_2-C_6HBr_3(SO_3H)$ [1:2:4:6:3]. From potassic tri-bromo-*m*-amido-benzoate by $KMnO_4$ (Rodatz, *A.* 215, 225). Flat orange needles. Reduced by $SnCl_2$ to the original $C_6H(NH_2)Br_3.SO_3H$.

$K_2A''3aq.$—$BaA''2aq.$—$CaA''7aq.$—$PbA''4aq.$

Chloride.—[222°-224°]. Dark violet tables.

Amide.—Brown crystals that do not melt.

Di-bromo-sulpho-benzene-azo-(β)-naphthol $C_6H_2Br_2(SO_3H)-N_2-C_{10}H_6OH$ (Stebbins, *C. N.* 42, 44; *A. C. J.* 2, 236). From diazo-dibromo-benzene sulphonic acid and an alkaline solution of (β)-naphthol.

Di-bromo-sulpho-benzene-azo-di-oxy-naphthalene $C_6H_2Br_2(SO_3H)-N_2-C_{10}H_5(OH)_2$. From diazo-dibromo-benzene sulphonic acid and an alkaline solution of dioxynaphthalene. Needles (Griess, *B.* 11, 2199).

Bromo-sulpho-toluene-azo-bromo-toluene sulphonic acid $N_2(C_6H_2BrMe.SO_3H)_2$ [1:?:4:5]. From potassic bromo-*p*-toluidine sulphonate (of Jenssen) and $KMnO_4$ (Kornatzki, *A.* 221, 186). Red tables with pointed ends. **Salts.**—$K_2A''4aq.$—$BaA''5aq.$—$CaA''4\frac{1}{2}aq.$—$PbA''5aq.$

Chloride.—[226°]. Groups of red prisms.

Amide.—[above 260°]: red powder.

Di-bromo-sulpho-toluene-azo-di-bromo-toluene sulphonic acid $N_2(C_6HBr_2Me.SO_3H)_2$ [1:?:?:2:5]. From potassic dibromo-*o*-toluidine sulphonate (of Hayduck) and $KMnO_4$ (Kornatzki, *A.* 221, 188). Blood-red plates. **Salts.**—$K_2A''2aq.$—$BaA''9aq.$—$CaA''8aq.$—$PbA''9aq.$

Chloride. [243°]. Red swallow-tailed plates.

Amide.—[218°]. Powder.

Di-butyl-*p*-amido-benzene-azo-di-butyl-aniline $(C_4H_9)_2N.C_6H_4-N_2-C_6H_4N(C_4H_9)_2$. *Di-butyl-aniline-azyline.* [158°]. Red needles. Formed by passing NO through an alcoholic solution of di-butyl-aniline.

Periodide.—B''_4I_6: dark crystals with blue reflection (Lippmann a. Fleissner, *B.* 15, 2142 and *B.* 16, 1421; *M.* 3, 713).

***m*-Carboxy-benzene-azo-aceto-acetic acid** $C_6H_4(CO_2H)-N_2-CHAc.CO_2H$. Formed by the action of the sulphate of *m*-diazo-benzoic acid upon acetoacetic ether in alkaline aqueous solution (Griess, *B.* 18, 962). Small yellow plates or needles. Soluble in alcohol, nearly insoluble in water. Bitter taste.

***o*-Carboxy-benzene-*o*-azo-benzoic acid** [2:1] $C_6H_4(CO_2H)-N_2-C_6H_4.CO_2H$ [1:2]. *o-Azo-benzoic acid.* [238°]. Mol. w. 270. From *o*-nitro-benzoic acid and sodium-amalgam (Griess, *B.* 10, 1868). Dark yellow hair-like needles. Insol. water; m. sol. alcohol.

Salts.—$BaA''7aq.$—$BaA''9aq.$—Ag_2A''.

Ethyl ether Et_2A''. [139°]. From *o*-nitro-benzoic ether by sodium-amalgam. Scarlet needles (Fittica, *J. pr.* [2] 17, 216).

***m*-Carboxy-benzene-*m*-azo-benzoic acid** $N_2(C_6H_4.CO_2H)_2$ [1:3]. *m-Azobenzoic acid.* From *m*-nitro-benzoic acid by sodium-amalgam (Strecker, *A.* 129, 134). Amorphous powder, decomposed by heat, v. sl. sol. water, alcohol, and ether. Gives phenazine when distilled with lime. Its copper salt gives azobenzene on distillation. HgO and iodine gives an amorphous di-iodo-derivative, $C_{14}H_8I_2N_2O_4$ (Benedikt *B.* 8, 386). **Salts.**—$BaA''5aq.$—Ag_2A''.

Ethyl ether Et_2A''. [99°]. By the action of EtI on Ag_2A'' Golubeff (*B.* 7, 1651) obtained two bodies isomeric with this ether, one melting at 76°, the other being a monobasic acid.

***p*-Carboxy benzene-*p*-azo-benzoic acid** $N_2(C_6H_4.CO_2H)_2$ [1:4]. From *p*-nitro-benzoic acid and sodium-amalgam (Beilstein a. Reichenbach, *A.* 129, 144; Bilfinger, *A.* 135, 154). Formed, together with azoxybenzoic acid, by boiling nitro-benzil with alcoholic KOH (Zinin, *Z.* 1868, 563). Flesh-coloured amorphous powder, insol. water, alcohol, and ether. Gives phenazine when distilled with lime. **Salts.**—$(NH_4)_2A''aq.$—Na_2A''.—$CaA''3aq.$—BaA''.—Ag_2A''.

Ethyl ether Et_2A''. [88°] (Fittica, *J. pr.* [2] 17, 216).

***m*-Carboxy-benzene-azo-malonic acid** $C_6H_4(CO_2H)-N_2-CH(CO_2H)_2$. Formed by the action of the nitrate of *m*-diazo-benzoic acid on malonic ether in alkaline aqueous solution (Griess, *B.* 18, 962). Microscopic orange needles or plates. Easily soluble in alcohol.

Carboxy-benzene-azo-di-methyl-amido-benzoic acid $C_6H_4(CO_2H).N_2.C_6H_3NMe_2.CO_2H$. From *m*-diazo-benzoic acid and dimethyl-*m*-amido-benzoic acid (Griess, *B.* 10, 525). Brown pp.

***m*-Carboxy-benzene-azo-nitro-methane** $C_6H_4(CO_2H).N_2.CH_2(NO_2)$. Formed by adding the nitrate of *m*-diazobenzoic acid to a dilute aqueous alkaline solution of nitromethane (Griess, *B.* 18, 961). Yellowish-red plates. Sol. hot alcohol and ether, v. sl. sol. water.

***m*-Carboxy-benzene-azo-(β)-naphthol** $C_6H_4(CO_2H)-N_2-C_{10}H_6(OH)$. [235°]. Prepared by the action of *m*-diazo-benzoic acid on an alkaline solution of (β)-naphthol (Griess, *B.* 14, 2035). Reddish-yellow needles or plates. Sol. hot alcohol, sl. sol. cold alcohol and ether, insol. water.

Salts: $A'_2Ba3\frac{1}{2}aq$: red microscopic needles. $A'K2aq$: easily soluble yellow needles or plates.

Ethyl ether A'Et. [104°]. Yellowish-red needles or plates. Sol. ether, insol. water.

Amide.—Slender orange needles. Sl. sol. alcohol and ether, insol. water.

***m*-Carboxy-benzene-azo-(β)-naphthol sulphonic acid** $C_6H_4(CO_2H)-N_2-C_{10}H_5(OH)(HSO_3)$. Prepared by the action of *m*-diazo-benzoic acid on an alkaline solution of (β)-naphthol sulphonic acid (Griess, *B.* 14, 2036). Brown needles or plates. Sol. hot water, sl. sol. cold water and alcohol, insol. ether. Dyes wool and silk a splendid orange.—A''_2H_2Ba4aq: orange pp. of slender needles.

***m*-Carboxy-benzene-azo-(β)-naphthol-di-sulphonic acid** $C_6H_4(CO_2H).N_2.C_{10}H_4(OH)(HSO_3)_2$. Prepared by the action of *m*-diazobenzoic acid on (β)-naphthol-(α)-disulphonic acid in alkaline solution (Griess, *B.* 14, 2037). Yellowish-red microscopic needles. Dyes silk and wool an orange scarlet.

Salts.—BaHA‴6aq: red crystalline pp.—$Ba_3A'''_2$12aq: red microscopic needles.

Carboxy-benzene-azo-phenol v. *Oxy-benzene-azo-benzoic acid.*

Di-carboxy-benzene-azo-phthalic acid $C_6H_3(CO_2H)_2—N_2—C_6H_3(CO_2H)_2$. *Azo-phthalic acid.* [about 250°]. Prepared by reduction of nitro-phthalic acid with sodium-amalgam (H. Müller; Claus a. May, *B.* 14, 1330). Small yellow needles: sl. sol. water, alcohol, and ether.

Salts.—$A^{iv}Na_4$10aq: yellow monoclinic prisms, v. sol. water.—$A^{iv}K_4$6aq: long yellow needles.—$A^{iv}Mg_2$18aq: large orange crystals.—$A^{iv}Ag_4$: yellow insoluble pp.—$A^{iv}Ba_2$: yellow insoluble pp.

Di-carboxy-benzene-azo-tere-phthalic acid [5:2:1] $C_6H_3(CO_2H)_2—N_2—C_6H_3(CO_2H)_2$ [1:5:2]. *Azo-terephthalic acid.*

Formation.—1. By oxidation of hydrazo-terephthalic acid with nitrous acid.—2. By reduction of nitro-terephthalic acid with sodium-amalgam (Homolka a. Löw, *B.* 19, 1092).

Yellow needles. Sol. alcohol and ether, sl. sol. water. Decomposes above 200°.

Carboxy-naphthalene-azo-(β)-naphthoic acid $C_{10}H_6(CO_2H)—N_2—C_{10}H_6(CO_2H)$. From a nitro-(β)-naphthoic acid by ammonium sulphide (Rakowsky, *B.* 5, 1022).

exo-**Carboxy-toluene-azo-phenyl-acetic acid** $CO_2H.CH_2.C_6H_4—N_2—C_6H_4.CH_2.CO_2H$. S. (cold alcohol) 0·375; (hot alcohol) 1·57. Insol. hot water, ether, and benzene. Does not melt below 300°. Formed by the action of sodium amalgam on nitro-phenyl-acetic acid [151] (Wittenberg, *Bl.* [2] 43, 111).

Carboxy-toluene-azo-toluic acid [5:2:1] $C_6H_3Me(CO_2H)—N_2—C_6H_3MeCO_2H$[1:5:2]. *Azo-p-toluic acid.* [184°]. From nitro-*p*-toluic acid by sodium amalgam (Fittica, *B.* 7, 1358). Minute yellow needles; m. sol. boiling water, v. sol. alcohol.

p-**Chloro-benzene-azo-benzene** *p*-**sulphonic acid** [4:1]$C_6H_4Cl—N_2—C_6H_4(SO_3H)$ [1:4] [148°]. Formed by warming *p*-chloro-azo-benzene with fuming sulphuric acid (10 p.c. SO_3) at 60°-70°. Brown needles; v. e. sol. water and alcohol. It is reduced by $SnCl_2$ to *p*-chloro-aniline and *p*-sulphanilic acid.

Salts.—A′Na: large orange-yellow pearly plates or small needles; sl. sol. cold water.—A'_2Ba: glistening flesh-coloured needles.—The K, Mg, Ca, Ag, Cr, and Fe, salts are white to dark-yellow needles; the Cu salt forms green plates; all are sparingly soluble.

Chloride $C_6H_4Cl.N_2.C_6H_4.SO_2Cl$: [130°]; glistening red prisms, easily soluble in alcohol and ether.

Amide $C_6H_4Cl.N_2.C_6H_4.SO_2NH_2$: [211°]; yellowish-brown prisms; sol. hot alcohol, sparingly in ether and cold alcohol, insol. water (Mentha a. Heumann, *B.* 19, 2972).

m-**Chloro-benzene-*m*-azo-chloro-benzene** [1:3] $C_6H_4Cl—N_2—C_6H_4Cl$ [1:3]. *Azo-chloro-benzene* [101°]. Obtained by acting with Fe_2Cl_6 on *m*-di-chloro-hydrazo-benzene in alcoholic solution (Laubenheimer, *B.* 8, 1025). Orange needles (from alcohol).

p-**Chloro-benzene-*p*-azo-chloro-benzene** [4:1] $C_6H_4Cl—N_2—C_6H_4Cl$ [1:4]. [181°]. From *p*-chloro-benzene-*p*-azo-nitro-benzene and alcoholic potash (Willgerodt, *B.* 15, 1002); or from di-chloro-azoxybenzene and fuming H_2SO_4 (Heumann, *B.* 5, 913, 918). Yellow needles.

p-**Chloro-benzene-azo-chloro-benzene sulphonic acid** [4:1] $C_6H_4Cl.N_2.C_6H_3Cl.SO_3H$ [1:4:?]. Prepared by sulphonation of the preceding body (Calm a. Heumann, *B.* 13, 1183; 15, 2558). Slender reddish-yellow needles. Sol. water and alcohol. Salts.—A′Na: golden plates, sl. sol. cold water.—A′K: reddish-yellow glistening plates, sol. hot water, and alcohol.—A′Ag.—A'_2Ba: yellow crystalline pp.—A'_2Ca: golden yellow plates.—A'_2Pb: orange glistening plates.

Chloride $C_{12}H_7Cl_2N_2SO_2Cl$: [161°]. Long orange-red needles.

Chloro-benzene-azo-chloro-phenol [3:1] $Cl.C_6H_4—N_2—C_6H_3Cl(OH)$ [1:3:?]. [115°] Formed by the action of fuming H_2SO_4 on *m*-di-chloro-azoxybenzene (Schultz, *B.* 17, 465). Brown plates.

Chloro-benzene-azo-chloro-nitro-benzene [4:1] $C_6H_4Cl—N_2—C_6H_3Cl(NO_2)$ [1:4:?]. [210°]. Prepared by reducing di-chloro-nitro-azoxybenzene with cold alcoholic NH_4HS (Calm a. Heumann, *B.* 13, 1184). Yellow needles. Sl. sol. alcohol.

m-**Chloro-benzene-azo-di-methyl-aniline** [3:1] $C_6H_4Cl—N_2—C_6H_4NMe_2$ [1:4]. [98°]. Yellow plates. Tolerably soluble in alcohol. Prepared by adding sodium nitrite (1 mol.) to a solution of *m*-chloraniline (1 mol.) and dimethylaniline (1 mol.) in dilute H_2SO_4 (Staedel a. Bauer, *B.* 19, 1955).

p-**Chloro-benzene-*p*-azo-nitro-benzene** [1:4] $C_6H_4Cl.N_2.C_6H_4(NO_2)$ [1:4]. [133°]. Formed by nitration of *p*-chloro-azo-benzene with fuming HNO_3. Yellow needles; v. sol. acetic acid and hot alcohol, sl. sol. cold alcohol, insol. water. It is reduced by $SnCl_2$ to *p*-chloro-aniline and *p*-phenylene diamine (Mentha a. Heumann, *B.* 19, 2971).

p-**Chloro-benzene-azo-phenol** $C_6H_4Cl—N_2—C_6H_4(OH)$. [152°]. Formed by gently warming *p*-chloro-diazo-benzene-chloro-anilide with phenol, *p*-chloraniline being eliminated. Reddish-yellow needles (Heumann a. Oeconomides, *B.* 20, 906).

Cumene-azo-cumene $PrC_6H_4—N_2—C_6H_4Pr$. *Azo-cumene.* [108°]. From nitro cumene, [−35°], by sodium-amalgam (Pospekhoff, *J. R.* 1886, 49). Thin yellow leaflets, sl. sol. cold alcohol.

ψ-Cumene-azo-ψ-cumenol [2:4:5:1] $C_6H_2(CH_3)_3.N_2.C_6H(CH_3)_3.OH$ [1:3:5:6:2]. [148°]. Formed by combining di-azo-cumene chloride (from ψ-cumidine) with ψ-cumenol [70°] (Liebermann a. Kostanecki, *B.* 17, 885). Orange needles. Insol. alkalis. Dissolves in H_2SO_4 with an orange colour. No nitrogen is evolved on boiling with HCl.

ψ-Cumene-azo-ψ-cumidine [2:4:5:1] $C_6H_2Me_3.N_2.C_6HMe_3.NH_2$ [1:2:4:5:6]. [139°]. Prepared by the action of cumidine hydrochloride upon diazo-cumene-cumide (di-azo-amido-cumene) dissolved in cumidine (Nölting a. Baumann, *B.* 18, 1147; *Bl.* [2] 42, 335). Orange plates (from alcohol). V. sol. ether. On reduction with $SnCl_2$ it yields cumidine and cumylene-*o*-diamine. Salt.—B′HCl: yellow crystalline powder; readily loses its HCl; dissolves in phenol with a yellowish-brown colour.

Cuminic-azo-cuminic acid $PrC_6H_3(CO_2H)—N_2—C_6H_3Pr.CO_2H$. [280°]. From

nitro-cuminic acid and sodium-amalgam (Alexéeff, *Bl.* [2] 38, 552; 42, 321; *J. R.* 1882, 198; Alexéeff a. Kissel, *Bl.* [2] 40, 72).

Ethers.—Me_2A''.[166°].—Et_2A''.[104°-108°].

Cymene-azo-cymene

$C_6H_3MePr—N_2—C_6H_3MePr$. [86°]. From nitro-cymene by sodium-amalgam (Werigo, *Z.* 1864, 721). Cherry-coloured plates.

Ethyl - amido - benzene - azo - benzene - *p* - sulphonic acid [4:1] $C_6H_4(SO_3H).N_2.C_6H_4.NHEt$ [1:4]. *p - Sulpho - benzene - azo - ethyl - aniline.* [c. 244°]. Obtained by combining *p*-diazo-benzene-sulphonic acid with ethyl-aniline in acid solution. Steel-blue needles. Nearly insol. alcohol and cold water, sl. sol. hot water. The sodium salt (NaA') forms orange-red plates. On reduction with $(NH_4)_2S$ it yields mono-ethyl-*p*-phenylene-diamine and *p*-sulphanilic acid (Bernthsen a. Goske, *B.* 20, 929).

Di-ethyl-*p*-amido-benzene-azo-di-ethyl-aniline $C_6H_4(NEt_2)-N_2—C_6H_4(NEt_2)$. *Di-ethyl-aniline-azyline.* [170°]. Prepared by passing NO through an alcoholic solution of di-ethyl-aniline; yield 50 p.c. of the theoretical. Red monoclinic crystals, $a:b:c = 1:.7108:.9493$. $\beta = 90° 30'$. V. sol. chloroform, sl. sol. cold alcohol.

Reactions.—1. *Nitrous acid* acting on the acetic solution gives *p*-nitro-di-ethyl-aniline.—2. On *reduction* it yields *u*-di-ethyl-*p*-phenylene-diamine.—3. Heated with *ethyl iodide* at 100° it gives tetra-ethyl-*p*-phenylene-diamine.—4. MeI at 100° gives di-methyl-di-ethyl-*p*-phenylene-diamine.

Salts.—$B''H_2Cl_2PtCl_4$: small brownish-red trimetric tables.—Ferrocyanide $B''_2H_4FeCy_6$: brown plates.—Picrate $B''(C_6H_2(NO_2)_3OH)_2$: yellow sparingly soluble needles (Lippmann a. Fleissner, *B.* 15, 2136; 16, 1415; *M.* 3, 286, 788).

Di-ethyl-amido-benzene-azo-toluidine

Acetyl derivative

[4:1] $C_6H_4(NEt_2)—N_2—C_6H_3Me(NHAc)$ [1:6:3]. [159°]. From diazotised acetyl-tolylene-diamine $C_6H_3(NH_2)Me(NHAc)$ [1:6:3] and di-ethyl-aniline (Wallach, *A.* 234, 359).

***o*-Ethyl-benzene-*o*-azo-ethyl-benzene**

[2:1]$C_6H_4(C_2H_5)—N_2—C_6H_4(C_2H_5)$[1:2].[47°corr.]. Formed by reduction of *o*-nitro-ethyl-benzene with zinc dust and alcoholic NaOH (Schultz, *B.* 17, 473). Long red dimetric prisms, $a:c = 1:.3455$. V. sol. alcohol. By treatment with $SnCl_2$ and HCl in alcoholic solution it yields a di-amido-di-ethyl-diphenyl.

***p*-Ethyl-benzene-*p*-azo-ethyl-benzene**

[4:1]$C_6H_4(C_2H_5)—N_2—C_6H_4(C_2H_5)$[1:4].[63°corr.]. (above 340°). Formed by reduction of *p*-nitro-ethyl-benzene with zinc-dust and alcoholic NaOH (Schultz, *B.* 17, 475). Orange-red plates or thick prisms. V. sol. alcohol. By treatment with $SnCl_2$ and H_2SO_4 in alcoholic solution it yields a di-amido-di-ethyl-diphenyl.

***p*-Ethyl-phenyl-amido-benzene-*p*-azo-ethyl-di-phenylamine**

[4:1] $C_6H_4NEtPh—N_2—C_6H_4NEtPh$ [1:4]. [178°]. From ethyl-di-phenyl-amine and NO (Lippmann a. Fleissner, *M.* 4, 796). Monoclinic red crystals.

Ethyl-pyrrol-azo-(β)-naphthalene

$C_{10}H_7.N_2.C_4H_3NEt$. [74°]. Obtained by adding (β)-diazo-naphthalene chloride (1 mol.) to ethyl-pyrrol (1 mol.) dissolved in alcohol containing sodium acetate. Thick red tables. Sparingly soluble in dilute HCl. Dissolves in conc. H_2SO_4 with a dark reddish-yellow colour. The platino-chloride forms small sparingly soluble red needles (O. Fischer a. Hepp, *B.* 19, 2258).

Ethyl-pyrrol-azo-*p*-toluene

$C_6H_4Me.N_2.C_4H_3NEt$ probably $C_6H_4Me.N_2.C{=}CH$, NEt, $HC{=}CH$ [62°]. Formed by adding *p*-diazo-toluene chloride (1 mol.) to an alcoholic solution of ethyl-pyrrol (1 mol.) containing sodium acetate. Thick red prisms. Dissolves in conc. H_2SO_4 with a yellow colour, in dilute HCl with a reddish yellow colour. The platino-chloride forms sparingly soluble red needles (O. Fischer a. Hepp, *B.* 19, 2257).

Iodo-carboxy-benzene-azo-iodo-benzoic acid

$C_6H_3I(CO_2H)—N_2—C_6H_3I(CO_2H)$. *Azo-iodo-benzoic acid.* From *m*-amido-benzoic acid, iodine, and HgO (Benedikt, *B.* 8, 386).

Mesitylene-azo-mesitylene

$C_6H_2(CH_3)_3—N_2—C_6H_2(CH_3)_3$. *Azo-mesitylene.* [75° corr.]. Prepared by oxidising an aqueous solution of mesidine hydrochloride (5 pts.) with a solution of 45 pts. of potassium ferricyanide and 10 pts. of KOH (Schultz, *B.* 17, 476). Thin red needles. Sol. hot alcohol. It does not appear to yield a hexa-methyl-benzidine by treatment with $SnCl_2$ and HCl in alcoholic solution.

Methyl-amido-benzene-azo-benzene-sulphonic acid[4:1] $C_6H_4(SO_3H).N_2.C_6H_4.NHMe$ [1:4]. *p-Sulpho-benzene-azo-methyl-aniline.* Obtained by combining *p*-diazo-benzene sulphonic acid with methyl-aniline in acid solution; yield 80 p.c. of theoretical. Also formed by the action of cold dilute acids upon *p*-sulpho-diazo-benzene-methyl-anilide $C_6H_4(SO_3H).N_2.NMeC_6H_5$. Steel blue needles, sl. sol. water. The sodium-salt (A'Na) forms large orange-red plates, v. sol. hot water. On reduction with $(NH_4)_2S$ it yields *p*-sulphanilic acid and mono-methyl-*p*-phenylene diamine (Bernthsen a. Goske, *B.* 20, 925).

Di-methyl-amido-benzene-azo-benzene-sulphonic acid [4:1] $C_6H_4(NMe_2)—N_2—C_6H_4SO_3H$ [1:4] *Helianthin, or Orange III.*

Preparation.—1. From dimethylaniline and *p*-diazobenzene sulphonic acid (Griess, *B.* 10, 525).—2. Dimethylamido-azobenzene (1 pt.) is dissolved in 20 pts. cold sulphuric acid of 30 p.c. anhydride value and allowed to stand for 24 hours (Möhlau, *B.* 17, 1491). The absorption spectrum has been mapped by Hartley (*C. J.* 51, 192).

Di-methyl-amido-benzene-azo-benzoic acid

[4:1] $C_6H_4NMe_2—N_2—C_6H_4.CO_2H$ [1:3]. From di-methyl-aniline and *m*-diazo-benzoic acid (Griess, *B.* 10, 525).

Di-methyl-amido-benzene-azo-di-methyl-aniline [1:4] $C_6H_4(NMe_2)—N_2—C_6H_4NMe_2$ [1:4] [266°]. *Dimethylaniline-azyline.* Red needles.

Formation.—1. By diazotising *p*-amido-di-methyl-aniline and combining the diazo-compound $C_6H_4(NMe_2).N_2.Cl$ with dimethylaniline (Nölting, *B.* 18, 1143).—2. By passing NO through an alcoholic solution of di-methyl-aniline for several days.

Reactions.—1. *Nitrous acid* acting on the acetic acid solution gives *p*-nitro-di-methyl-aniline.—2. On *reduction* it gives *u*-di-methyl-*p*-phenylene-diamine.

Salts.—$B''H_2Cl_2PtCl_4$: dichroic crystalline powder.—**Picrate** $B''C_6H_2(NO_2)_3OH + C_2H_5OH$: glistening green needles (Lippmann a. Fleissner, *B.* 15, 2136; 16, 1415; *M.* 3, 708).

Di-methyl-amido-benzene-azo-*p*-toluene $C_7H_7—N_2—C_6H_4.NMe_2$. [168°]. Golden plates. Easily soluble in alcohol and ether.

Preparation.—A solution of 65 pts. of $NaNO_2$ (100 p.c.) and 35 pts. NaOH in 465 pts. of water is slowly added to a cooled solution of 100 pts. of *p*-toluidine, 113 pts. of dimethylaniline and 200 pts. of HCl in 300 pts. of water.

On reduction it yields *p*-toluidine and di-methyl-*p*-phenylene-diamine. The hydrochloride and sulphate form violet prisms, giving a red solution in alcohol (Möhlau, *B.* 17, 1492).

Di-methyl-amido-benzene-azo-*p*-toluene-sulphonic acid $C_7H_6(HSO_3).N_2.C_6H_4.NMe_2$. Formed by the combination of *p*-diazo-toluene sulphonic acid ($Me:HSO_3:N_2 = 1:3:4$) with dimethylaniline (Möhlau, *B.* 17, 1493). Dark-violet prisms. Soluble in water and alcohol with an orange colour, insoluble in ether. The sodium salt forms orange glistening plates.

Di-methyl-amido-benzene-azo-toluidine [4:1] $C_6H_4(NMe_2)—N_2—C_6H_3Me(NH_2)$ [1:6:3] [145°]. From its acetyl derivative [200°] which is formed by the action of diazotised-acetyl-tolylene-diamine $C_6H_3(NH_2)Me(NHAc)$ [1:6:3] upon di-methyl-aniline (Wallach, *A.* 234, 355).

Di-methyl-amido-benzene-azo-toluidine [4:1] $C_6H_4(NMe_2)—N_2—C_6H_3Me(NH_2)$ [1:4:3] [215°]. From its acetyl derivative, [192°] which is formed by the action of diazotised acetyl-tolylene-diamine $C_6H_3(NH_2)Me(NHAc)$ [1:4:3] upon di-methyl-aniline (Wallach, *A.* 234, 359).

***p*-Methyl-phenyl-amido-benzene-azo-methyl-di-phenyl-amine** [4:1] $C_6H_4NMePh.N_2.C_6H_4NMePh$ [1:4] [150°]. Yellow crystals, got by the action of NO on methyl-diphenyl-amine (Lippmann a. Fleissner, *M.* 4, 798).

(α)-Naphthalene-(α)-azo-naphthalene [α] $C_{10}H_7.N_2.C_{10}H_7$ [α]. [190°]. Prepared by boiling diazo-naphthalene-azo-naphthalene with alcohol: 1 pt. of naphthalene-azo-naphthylamine is dissolved in 100 pts. of 95 p.c. alcohol and 5 pts. of H_2SO_4 are added; the still warm solution is then treated with a saturated solution of (1 mol. of) $NaNO_2$; the fluid is heated and finally boiled for a few hours, and the azonaphthalene precipitated by water. It is recrystallised by dissolving it in hot aniline and adding alcohol (Nietzki a. Goll, *B.* 18, 298, 3252). Steel-blue crystals. Sublimes in thin yellow plates. Soluble in aniline, sparingly in alcohol. It dissolves in cold H_2SO_4 with a blue colour, but on heating the solution to about 180° it becomes violet and exhibits a red fluorescence. By alcoholic NH_4HS, or zinc-dust and alcoholic KOH, it is reduced to hydrazonaphthalene.

(α)-naphthalene-(β)-azo-naphthalene [α]$C_{10}H_7.N_2.C_{10}H_7$[β]. [136°]. Obtained by diazotisation of (β)-naphthalene-*p*-azo-(α)-naphthylamine and boiling with alcohol. Dark-brown plates with steel-blue reflex. Sol. alcohol, acetic acid, &c. Dissolves in conc. H_2SO_4 with a violet colour (Nietzki a. Göttig, *B.* 20, 612). Laurent's **naphthase** [275°], got by heating nitro-naphthalene with zinc dust, or (α)-naphthylamine with PbO, has been regarded as naphthalene-azo-naphthalene, but Witt has lately (*B.* 19, 2794) shown it to be an azine $C_{20}H_{12}N_2$ *v.* (αβ)-NAPHTHAZINE (Laurent, *A.* 109, 384; Doer, *B.* 3, 291; Alexéeff, *B.* 3, 868; Schichuzky, *B.* 5, 365; Klobulowsky, *B.* 10, 570, 772, 873).

Naphthalene-*p*-azo-(α)-naphthol $C_{10}H_7—N_2—C_{10}H_6OH$. Formed by adding diazo-naphthalene chloride to a solution of (α)-naphthol in NaOHAq; it is ppd. by HCl. Crimson powder. Soluble in alkalis forming crimson solutions (P. F. Frankland, *C. J.* 37, 752).

Naphthalene-*o*-azo-(β)-naphthol $C_{10}H_7—N_2—C_{10}H_6OH$. [176°]. Formed by diazotising (β)-amido-azo-naphthalene and heating the diazo- compound with water (Nietzki a. Goll, *B.* 19, 1282). Sublimes in glistening golden needles.

(α)-Naphthalene-(α)-azo-(α)-naphthylamine $C_{10}H_7—N_2—C_{10}H_6.NH_2$. [180°]. Prepared by adding KNO_2 (1 mol.) to a dilute solution of (α)-naphthylamine hydrochloride (2 mol.) and making the mixture slightly alkaline with Na_2CO_3 (Perkin a. Church, *A.* 129, 108; Nietzki a. Goll, *B.* 18, 298). Hartley (*C. J.* 51, 190) has mapped the absorption-spectrum.—B'_4HCl.—$B'HCl$.—$B'2HCl$.—$B'_2H_2SO_4$.

(β)-Naphthalene-*p*-azo-(α)-naphthylamine $C_{10}H_7.N_2.C_{10}H_6.NH_2$ [152°]. Formed by mixing aqueous solutions of equal mols. of (β)-diazo-naphthalene chloride (from (β)-naphthylamine) and (α)-naphthylamine hydrochloride. Yellowish-brown needles with green reflex (from alcohol). The base and its salts are far more soluble than the (α)-azo-(α)-naphthalene. H_2SO_4 dissolves it with a violet colour (Nietzki a. Göttig, *B.* 20, 612).

(β)-Naphthalene-azo-(β)-naphthylamine

$$C_{10}H_6\left\langle\begin{array}{l}NH\\ |\\ N_2H.C_{10}H_7\end{array}\right. \quad \text{or } C_{10}H_7.N_2.C_{10}H_6.NH_2 \ [149°].$$

Reddish-yellow needles. Easily soluble in benzene and acetic acid, insoluble in water. Formed by the action of amyl nitrite upon (β)-naphthylamine. The absorption-spectrum has been mapped by Hartley (*C. J.* 51, 191).

Reactions.—1. By heating with dilute H_2SO_4 (20 p.c.) it is decomposed with evolution of nitrogen.—2. On reduction with $SnCl_2$ it yields (β)-naphthylamine and (1:2)-naphthylenediamine.—3. Treated with *bromine* in alcoholic or acetic acid solution it is converted into di-bromo-(β)-naphthylamine and a brominated β-naphthol. 4. May be *diazotised* in the following manner: 15 grms. of the amidoazonaphthalene are finally suspended in a mixture of 90 grms. H_2SO_4 and 90 grms. of water, cooled with ice and slowly treated with a concentrated solution of 5 grms. sodium nitrite. The diazo- compound is very unstable (Nietzki a. Goll, *B.* 19, 1281).

Acetyl derivative $C_{20}H_{14}N_3Ac$ [218°]; prisms; easily soluble in benzene, sparingly in alcohol and petroleum-spirit.

Benzoyl derivative $C_{20}H_{14}N_3Bz$ [177°]; silky red needles; easily soluble in benzene, sparingly in alcohol and petroleum-spirit (Lawson, *B.* 18, 2422).

(α)-Naphthalene-azo-*peri*-naphthylene-diamine $C_{10}H_7—N_2—C_{10}H_5(NH_2)_2$. Prepared by the action of (α)-diazonaphthalene chloride on *peri*-naphthylene-diamine (Stebbins, jun., *B.* 13,

717; *C. N.* 41, 117; *A. C. J.* 1, 445). Sol. alcohol, insol. water.—B'HCl: sl. sol. water, m. sol. alcohol with a brown colour; dissolves in strong H_2SO_4 with a blue colour.

(β)-Naphthol-azo-naphthalene sulphonic acid $C_{10}H_6(OH)—N_2—C_{10}H_6SO_3H$. From (β)-naphthol and (α)-diazo-naphthalene sulphonic acid (W. v. Miller, *B.* 13, 268).

(α)-Naphthol-*p*-azo-diphenyl sulphonic acid $C_{10}H_6(OH)—N_2—C_{12}H_8.SO_3H$. From (α)-naphthol and *p*-diazo-diphenyl sulphonic acid (Carnelley a. Schlevelmann, *C. J.* 49, 383).—NaA': dyes wool brown—BaA'$_2$.

(β)-Naphthol-*p*-azo-diphenyl sulphonic acid $C_{10}H_6(OH)—N_2—C_{12}H_8.SO_3H$. From (β)-naphthol and *p*-diazo-diphenyl sulphonic acid.—NaA': bright red pp., sl. sol. cold, v. sol. hot, water; dyes wool red.—BaA'$_2$ (Carnelley a. Schlevelmann, *C. J.* 49, 383).

***o*-Nitro-benzene-azo-aceto-acetic acid** $C_6H_4(NO_2)—N_2—CH(CO.CH_3).CO_2H$. [185°]. Obtained by saponification of the ethyl-ether which is prepared by the action of *o*-nitro-diazo-benzene chloride on an alkaline solution of aceto-acetic ether (Bamberger, *B.* 17, 2415). Glistening brown plates. V. sol. acetic acid and hot alcohol, v. sl. sol. ether and cold alcohol. On heating it evolves CO_2 and yields *o*-nitro-benzene-azo-acetone $C_6H_4(NO_2).N_2.CH_2.CO.CH_3$. The same decomposition is produced by heating with alkalis.

S a l t s.—A'NH$_4$^{x}: yellow needles.—A'Ag: crystalline pp.—A'$_2$Cu^x: green pp., sol. hot water.—A'$_2$Ba^x: yellow needles.—A'$_2$Hg: glistening plates.

Ethyl ether A'Et [93°], glistening yellow plates or fine needles, sol. alcohol, ether, acetic acid, and hot water.

***o*-Nitro-benzene-azo-acetone** $C_6H_4(NO_2)—N_2—CH_2.CO.CH_3$. [124°]. Formed by heating *o*-nitro-benzene-azo-aceto-acetic acid to its melting-point, or by boiling the acid or its ether with alkalis.

Preparation.—*o*-Nitraniline dissolved in absolute alcohol is diazotised by passing into the well-cooled solution a stream of N_2O_3, the product is poured into iced water, the solution filtered and mixed without cooling with a dilute solution of acetacetic ether (1 mol.), and KOH (1 mol.), after mixing the fluid must be acid, it is digested at about 40° for 40 hours, the red pp. is then filtered off and purified (Bamberger, *B.* 17, 2418). Long silky yellow needles. Easily soluble in hot water, alcohol, ether, &c.

***o*-Nitro-benzene-azo-acetophenone** [2:1] $C_6H_4(NO_2)—N_2—CH_2.CO.C_6H_5$. [141°]. Formed together with *o*-nitro-benzene-azo-benzoyl-acetic ether, by adding a solution of *o*-nitro-diazo-benzene chloride to an iced alkaline solution of benzoyl-acetic ether (Bamberger a. Calman, *B.* 18, 2565). Glistening yellow needles. Easily soluble in ordinary solvents.

***m*-Nitro-benzene-azo-aniline** [3:1] $NO_2.C_6H_4.N_2.C_6H_4.NH_2$ [1:4]. [c. 210°]. From diazotised *m*-nitraniline hydrochloride and aniline hydrochloride (Meldola, *C. J.* 45, 112). Orange fern-like leaflets (from alcohol). Insol. water and dilute acids; forms yellow solutions in alcohol, acetone, and benzene (Meldola, *C. J.* 45, On reduction it gives *m*- and *p*-phenylene-diamine. S a l t.—(B'HCl)$_2$PtCl$_6$.

Nitro-benzene-azo-benzene sulphonic acid [3:1] $C_6H_4(NO_2)—N_2—C_6H_4SO_3H$ [1:4]. From benzene-azo-benzene sulphonic acid by nitration (Janovsky, *M.* 3, 505; 8, 60).—KA'.—BaA'$_2$.—PbA'$_2$.

Nitro-benzene-azo-benzene sulphonic acid [4:1] $C_6H_4(NO_2)—N_2—C_6H_4.SO_3H$ [1:4]. Formed, together with the less soluble isomeride just described, by heating benzene-azo-benzene *p*-sulphonic acid with nitric acid (S.G. 1·41). Leaflets.—KA' (Janovsky, *M.* 3, 506; 5, 157; *B.* 16, 1486). Ammonium sulphide reduces it to an amido-benzene-azo-benzene sulphonic acid which is different from that formed from diazotised sulphanilic acid and *p*-phenylene-diamine, although on complete reduction it gives sulphanilic acid and *p*-phenylene-diamine.

Di-nitro-benzene-azo-benzene-sulphonic acid [3:4:1] $C_6H_3(NO_2)_2—N_2—C_6H_4.SO_3H$ [1:4]. From either of the two preceding acids or from benzene-azo-benzene sulphonic acid and nitric acid (S.G. 1·45). Orange leaflets.—KA'.—BaA'$_2$: S. 7 at 68° (Janovsky, *M.* 3, 507; 5, 157).

***o*-Nitro-benzene-azo-benzoyl-acetic acid** [2:1]$C_6H_4(NO_2)—N_2—CH(CO.C_6H_5).CO_2H$.[177°] Its ethyl-ether is formed, together with *o*-nitro-benzene-azo-acetophenone, by adding a solution of *o*-nitro-diazo-benzene chloride to an iced alkaline solution of benzoyl-acetic ether (Bamberger a. Calman, *B.* 18, 2565). Long, yellow silky needles. Sl. sol. alcohol and ether. By long heating at its melting-point it loses CO_2 giving *o*-nitro-benzene-azo-acetophenone.

Oxim $C_{14}H_{10}N_2(NO_2)(CO_2H)NOH$ [142°]; orange-yellow needles.

***m*-Nitro-benzene-azo-*m*-chloro-di-methyl-aniline** [3:1] $C_6H_4(NO_2).N_2.C_6H_3Cl.NMe_2$ [1:2:4] [156°]. Prepared by adding sodium nitrite (1 mol.) to a solution of *m*-nitraniline (1 mol.) and *m*-chloro-di-methyl-aniline (1 mol.) in dilute H_2SO_4 (Staedel a Bauer, *B.* 19, 1956). Reddish-yellow plates (from alcohol).

***p*-Nitro-benzene-azo-di-methylaniline** [4:1] $NO_2.C_6H_4.N_2.C_6H_4NMe_2$ [1:4]. [230°]. The hydrochloride is deposited as crystals with steel-blue reflex when aqueous diazo-*p*-nitro-benzene chloride is added to aqueous dimethylaniline hydrochloride (Meldola, *C. J.* 45, 107).

Properties.—Chocolate-brown powder, slightly soluble in alcohol whence it separates as brown needles. Solutions are orange in benzene and in glacial acetic acid, orange in conc. H_2SO_4, red on dilution. S a l t.—(B'HCl)$_2$PtCl$_4$.

***m*-Nitro-benzene-*p*-azo-dimethylaniline** [3:1] $NO_2.C_6H_4.N_2.C_6H_4NMe_2$ [1:4]. [159°]. From $NO_2.C_6H_4N_2Cl$ and $C_6H_5NMe_2HCl$ (Meldola, *C. J.* 45, 120; Staedel a. Bauer, *B.* 19, 1954). Orange crystalline powder. Solutions in alcohol, benzene, acetone, and glacial acetic acid, are yellowish-orange; in conc. H_2SO_4 pale orange, turned red by dilution. After reduction by HCl and zinc-dust, Fe_2Cl_6 forms a blue dye.

***m*-Nitro-benzene-azo-(α)-naphthol** [3:1] $C_6H_4(NO_2)—N_2—C_{10}H_6OH$ [1:4]. From *m*-diazo-nitro-benzene and (α)-naphthol (Stebbins, jun., *A. C. J.* 2, 446). Brown pp., sol. water.

***p*-Nitro-benzene-azo-(α)-naphthol** [4:1] $C_6H_4(NO_2)—N_2—C_{10}H_6OH$ [1:4]. From *p*-diazo-nitro-benzene chloride and an alkaline solution of (α)-naphthol (Meldola, *C. J.* 47, 661). Dull red powder, melts above 360°. V. sl. sol.

iling alcohol. H_2SO_4 forms a violet solution; t NaOHAq gives a blue colour.

m-**Nitro-benzene-azo-(β)-naphthol**
:1] $C_6H_4(NO_2)-N_2-C_{10}H_6OH$ [1:2] or

$$C_{10}H_6\left\langle\begin{matrix}O\\|\\N_2.H.C_6H_4(NO_2)\end{matrix}\right.$$

[194°]. From *m*-diazo-itro-benzene chloride and an alkaline solution f (β)-naphthol (Meldola, *C. J.* 47, 668). Lustrous range scales (from toluene). Insol. aqueous lkalis; sol. alcoholic KOH. H_2SO_4 gives a agenta red solution. It is not reduced by ammonium sulphide.

p-**Nitro-benzene-azo-(β)-naphthol**
[4:1] $C_6H_4(NO_2)-N_2-C_{10}H_6OH$ (?) [1:2]. [249°]. From *p*-diazo-nitro-benzene chloride and sodium (β)-naphthol (Meldola, *C. J.* 47, 663). Orange needles. Insol. hot NaOHAq. Conc. H_2SO_4 gives a magenta-red solution.

m-**Nitro-benzene-azo-(β)-naphthol-disulphonic acid** [3:1]$C_6H_4(NO_2).N_2.C_{10}H_4.(SO_3H)_2(OH)$ (?). Prepared by acting on di-azo-*m*-nitro-benzene with (β)-naphthol disulphonic acid in alkaline solution. V. sol. water; dyes an old gold colour (Stebbins, jun., *A. C. J.* 2, 446).

m-**Nitro-benzene-(α)-azo-(α)-naphthylamine**
[3:1] $NO_2.C_6H_4-N_2-C_{10}H_6.NH_2$ [1:4]. [203°]. From $NO_2.C_6H_4N_2Cl$ and $C_{10}H_7NH_2HCl$ (Meldola, *C. J.* 45, 114).

Properties.—Red needles. Solutions in alcohol, acetone, and benzene, are orange; in acetic acid, red; in conc. H_2SO_4 violet-red turned red by dilution. Completely decomposed by ammonic sulphide.

p-**Nitro-benzene-azo-(α)-naphthylamine**
[4:1] $NO_2.C_6H_4.N_2.C_{10}H_6.NH_2$ [1:4]. [252°]. From aqueous *p*-nitro-diazo-benzene chloride and alcoholic (α)-naphthylamine hydrochloride (Meldola, *C. J.* 43, 430). Brown needles (from benzene). Forms a crimson alcoholic solution. $(B'HCl)_2PtCl_4$. Salts hardly soluble in alcohol.

Reactions.—Reduces to *p*-phenylene-diamine and (α,α) naphthylene-diamine.

m-**Nitro-benzene-azo-(β)-naphthylamine**
[3:1] $C_6H_4(NO_2)-N_2-C_{10}H_6(NH_2)$ or

$$\left.\begin{matrix}NH\\|\\C_6H_4(NO_2)-N_2H\end{matrix}\right\rangle C_{10}H_6.$$

[177°]. From $NO_2.C_6H_4.N_2Cl$ and (β)-naphthylamine. Splendid orange needles. Solutions in toluene, chloroform, and glacial acetic acid, are orange; in alcohol and in acetone, orange but turned red by HCl; in conc. H_2SO_4, violet (Meldola, *C. J.* 45, 117).

p-**Nitro-benzene-azo-(β)-naphthylamine**
[4:1] $NO_2.C_6H_4-N_2-C_{10}H_6NH_2$ (?) [1:2]. [180°]. From aqueous *p*-nitro-diazo-benzene chloride and aqueous (β)-naphthylamine hydrochloride (Meldola, *C. J.* 43, 420). Needles, with golden lustre (from alcohol). Its solutions in alcohol, acetone, and chloroform are red, in benzene and toluene, orange, in conc. H_2SO_4, violet. Its salts are readily soluble in alcohol.—$(B'HCl)_2PtCl_4$.

p-**Nitro-benzene-azo-*p*-nitro-benzene**
[4:1] $C_6H_4(NO_2)-N_2-C_6H_4(NO_2)$ [1:4]. *Di-nitro-azo-benzene.* [204°]. Formed by nitration of benzene-azo-benzene (Laurent a. Gerhardt, *A.* 75, 73; Janovsky, *M.* 6, 159; 7, 135; *B.* 18, 1134). Red crystals (from glacial HOAc). Gives, when reduced by ammonium sulphide, a nitrolic acid $(C_6H_4(NO_2)-N_2-C_6H_4{:}NOH)_2$ (?) [218°] of which the sodium salt is blue. It is re-oxidised by K_3FeCy_6 to *p*-nitro-benzene-azo-*p*-nitro-benzene.

m-**Nitro-benzene-azo-*m*-nitro-benzene**
[3:1] $C_6H_4(NO_2)-N_2-C_6H_4(NO_2)$ [1:3]. A red oil, formed in the preparation of the preceding (Janovsky, *M.* 6, 455). Ammonium sulphide and NaOH give a violet colour.

o-**Nitro-benzene-*p*-azo-nitro-benzene**
[2:1] $C_6H_4(NO_2)-N_2-C_6H_4(NO_2)$ [1:4]. [208°]. From nitro-benzene-*o*-azo-nitro-benzene (Janovsky, *M.* 7, 131). Orange laminæ. Alcoholic ammonium sulphide mixed with NaOHAq gives a permanent blue.

Nitro-benzene-azo-nitro-benzene
$C_6H_4(NO_2)-N_2-C_6H_4(NO_2)$ [1:4]. [205°]. A by-product in the nitration of benzene-azo-benzene-*p*-sulphonic acid (Janovsky, *M.* 7, 132). Orange laminæ. Ammonium sulphide and NaOH gives a permanent blue nitrolate.

Nitro-benzene-azo-nitro-benzene
$C_6H_4(NO_2)-N_2-C_6H_4(NO_2)$. [180°]. A product of nitration of benzene-azo-benzene (Janovsky, *M.* 7, 134). Pale, asbestos-like, needles. Ammonium sulphide and NaOH give a blue nitrolate changing to brown.

Nitro-benzene-azo-di-nitro-benzene
[4:1] $C_6H_4(NO_2)-N_2-C_6H_3(NO_2)_2$ [1:2:3 or 5 or 6] or [1:3:5]. [112°]. Formed by nitration of benzene-azo-benzene (Petrieff, *Z.* [2] 6, 564) or benzene-azo-*p*-nitro-benzene (Janovsky, *M.* 7, 125). Yellow needles. Boiling with a mixture of alcoholic NaOH and aqueous ammonium sulphide gives a green colour, changing to brown.

Nitro-benzene-azo-di-nitro-benzene
[3:1] $C_6H_4(NO_2)-N_2-C_6H_3(NO_2)_2$ [1:3:4]. [170°]. Formed by nitration of benzene-*p*-azo-nitro-benzene or *m*-nitro-benzene-*m*-azo-nitro-benzene (Janovsky, *M.* 7, 126). Yellow tables. Alcoholic ammonium sulphide and aqueous NaOH give an olive-green colour, turning brown.

Nitro-benzene-azo-di-nitro-benzene
[3:1]$C_6H_4(NO_2)-N_2-C_6H_3(NO_2)_2$[1:3:2 or 5 or 6]. [121°]. Formed by nitrating *m*-nitro-benzene-*m*-azo-nitro-benzene (J.). Yellow prisms. Nitrolic reaction: emerald-green changing to orange.

Nitro-benzene-azo-di-nitro-benzene
[4:1] $C_6H_4(NO_2)-N_2-C_6H_3(NO_2)_2$ [1:4:3 or 2]. [185°]. Formed by nitrating *p*-nitro-benzene-*p*-azo-nitro-benzene or benzene-azo-benzene (Janovsky, *M.* 6, 461; *B.* 18, 1135). Needles.

Nitro-benzene-azo-di-nitro-benzene
[4:1] $C_6H_4(NO_2)-N_2-C_6H_3(NO_2)_2$ [1:4:2 or 3]. [160°]. Formed in the preparation of the preceding substance (Janovsky, *M.* 6, 462; 7, 125; *B.* 18, 1134). Yellow needles (from alcohol). Nitrolic reaction: green, turning blue. This body and the preceding, both give (1, 2, 4)-tri-amido-benzene and *p*-phenylene-diamine on reduction.

Nitro-benzene-azo-nitro-ethane
[3:1]$C_6H_4(NO_2)-N_2-CH(NO_2).CH_3$. From potassium nitro-ethane and *m*-diazo-nitro-benzene nitrate (Hallmann, *B.* 9, 391). Yellow powder. Reduced by tin and HCl to the tin salt $B''H_2SnCl_6$ of an unstable base di-amido-phenyl-ethyl-hydrazine $C_6H_4(NH_2)-N_2H_2-CH(NH_2).CH_3$.

Nitro-benzene-azo-nitro-phenol
[3:1]$C_6H_4(NO_2).N_2.C_6H_2(NO_2)(OH)$[1:3:4?].[173°]. Formed by heating the isomeric di-*m*-nitro-azoxy-benzene $C_6H_4(NO_2)-N_2O-C_6H_4(NO_2)$

with strong H_2SO_4 for some time to about 140° (Klinger a. Pitschke, *B.* 18, 2552). Yellowish-brown crystals. Dissolves in alkalis with an orange colour.—A'Ag: red crystalline pp.

p-Nitro-benzene-azo-o-oxy-benzoic acid [4:1] $C_6H_4(NO_2)-N_2-C_6H_3(CO_2H)(OH)$ [1:3:4]. From diazotised *p*-nitro-aniline and a cooled alkaline solution of salicylic acid (Meldola, *C. J.* 47, 666). Brown needles (from dilute acetic acid); sol. alkalis. H_2SO_4 gives an orange solution. Blackens at 225°.

p-Nitro-benzene-azo-phenol [4:1] $C_6H_4(NO_2)-N_2-C_6H_4OH$ [1:4]. [184°]. From diazotised *p*-nitro-aniline and sodium phenol (Meldola, *C. J.* 47, 658). Golden scales; v. sl. sol. water; sol. boiling dilute alkalis. H_2SO_4 gives an orange solution.

m-Nitro-benzene-p-azo-diphenylamine [3:1] $(NO_2)C_6H_4-N_2-C_6H_4(NHC_6H_5)$ [1:4]. [137°]. From $NO_2C_6H_4N_2Cl$ and $NH(C_6H_5)_2$ (Meldola, *C. J.* 45, 118). Reddish-brown scales (from dilute alcohol). Solutions in alcohol, acetone, glacial acetic acid, and benzene are orange. On adding HCl to the alcoholic solution the liquid turns crimson, and, if concentrated, a brown gelatinous hydrochloride is ppd. Conc. H_2SO_4 forms a violet solution. After reduction by Zn and HCl, Fe_2Cl_6 forms a blue dye. Its salts are unstable.

Nitroso derivative [128°].

p-Nitro-benzene-azo-di-phenylamine [4:1]$(NO_2)C_6H_4-N_2-C_6H_4(NH.C_6H_5)$[1:4] [151°]. From aqueous diazotised *p*-nitraniline and alcoholic diphenylamine. The pp. is treated with ammonium carbonate, and the base crystallised from dilute alcohol (Meldola, *C. J.* 43, 440). Brown leaflets. Solutions are orange in alcohol, turned violet by HCl; violet in conc. H_2SO_4. The hydrochloride forms needles, with violet reflex, but is very unstable.

p-Nitro-benzene-azo-resorcin [4:1] $C_6H_4(NO_2)-N_2-C_6H_3(OH)_2$ [1:2:4]. From *p*-diazo-nitro-benzene nitrate and resorcin in alkaline solution (Meldola, *C. J.* 47, 660). Brick-red crystalline powder; KOHAq forms a violet, H_2SO_4 an orange, solution.

p-Nitro-benzene-azo-m-xylidine [4:1] $(NO_2).C_6H_4-N_2-C_6H_2Me_2(NH_2)$ [1:3:5:2]. [141°]. From aqueous *p*-nitro-diazo-benzene chloride and alcoholic *m*-xylidine hydrochloride (Meldola, *C. J.* 43, 428). There results a bulky reddish pp. of $NO_2.C_6H_4.N_2.NHC_6H_3Me_2$ which, on standing, changes to the scarlet hydrochloride of the azo- compound.

Properties.—Brick-red needles (from dilute alcohol). Forms orange solutions in alcohol, acetone, benzene, chloroform, and conc. H_2SO_4.

Salts.—The chloride, sulphate, and nitrate form red needles with violet reflex, insoluble in alcohol.—$(B'HCl)_2PtCl_4$.

Nitro-carboxy-benzene-azo-nitro-benzoic acid $N_2(C_6H_3(NO_2).CO_2H)_2$(?). Formed by nitrating carboxy-benzene-azo-benzoic acid (Golubeff, *J. R.* 6, 197).—Na_2A''.—K_2A'' 3aq.—BaA''.—Et_2A'': [104°].

Di-nitro-oxy-amido-benzene-azo-xylene $C_6H(NO_2)_2(NH_2)(OH)-N_2-C_6H_3Me_2$. From diazo-xylene chloride and di-nitro-amido-phenol in alkaline solution (Stebbins, jun., *A. C. J.* 2, 236). Brown powder, sl. sol. cold water.

Nitro-oxy-benzene-azo-benzene sulphonic acid [3:4:1]$C_6H_3(NO_2)(OH)-N_2-C_6H_4.SO_3H$[1:4]. From diazotised sulphanilic acid and *o*-nitro-phenol (Griess, *B.* 11, 2195; R. Meyer a. Kreis, *B.* 16, 1331).

Nitro - oxy - benzene - azo - naphthalene sulphonic acid $C_6H_3(NO_2)(OH)-N_2-C_{10}H_6.SO_3H$. From diazotised (α)-naphthylamine sulphonic acid and *o*-nitro-phenol (Stebbins, jun., *A. C. J.* 2, 236). Red needles, v. sol. water.

Di-nitro-oxy-benzene-azo-napthylamine sulphonic acid $C_6H_2(NO_2)_2(OH).N_2.C_{10}H_5(NH_2).SO_3H$. From diazo-di-nitro-phenol and (α)-naphthylamine sulphonic acid (Stebbins, jun., *A. C. J.* 2, 446). Reddish-brown dye; sol. water.

Nitro-oxy-benzene-azo-nitro-phenol.

Ethyl ether [2:x:1]$C_6H_3(OEt)(NO_2).N_2.C_6H_3(OEt)(NO_2)$[1:2:x]. [190°]. Formed by nitrating *o*-oxy-benzene-*o*-azo-phenol ethyl ether, and separated from the isomeric compound by alcohol, in which it dissolves (Andreae, *J. pr.* [2] 21, 322). Needles (from alcohol).

Nitro-oxy-benzene-azo-nitro-phenol.

Ethyl ether [2:x:1]$C_6H_3(OEt)(NO_2).N_2.C_6H_3(OEt)(NO_2)$[1:2:x]. [285°]. Formed together with the preceding (*q. v.*). Brownish-red crystals (from chloroform). Insol. alcohol. Dissolves without change in conc. H_2SO_4. Reduced by alcoholic ammonium sulphide to the di-ethyl ether of dinitro-dioxy-di-phenyl-hydrazine.

Di-nitro-oxy-benzene-azo-phenol sulphonic acid $C_6H_2(NO_2)_2(OH)-N_2-C_6H_3(OH).SO_3H$. From diazotised di-nitro-amido-phenol and an alkaline solution of phenol *o*-sulphonic acid (Stebbins, jun., *A. C. J.* 2, 236; *C. N.* 42, 44). Brown lustrous needles, sl. sol. hot water.

Nitro-diphenyl-azo-nitro-diphenyl (?) [4:1] $C_6H_4(NO_2).C_6H_4-N_2-C_6H_4.C_6H_4(NO_2)$ [1:4]. [187°]. From *p*-dinitro-diphenyl and sodium amalgam (Wald, *B.* 10, 137). Yellow powder (from alcohol).

m-Nitro-toluene-azo-aceto-acetic acid [4:2:1] $C_6H_3(CH_3)(NO_2)-N_2-CH(CO.CH_3).CO_2H$ [176°]. Obtained by saponification of the ethyl-ether formed by the action of nitro-diazo-toluene chloride (from nitro-*p*-toluidine [114°]) on an alkaline solution of aceto-acetic ether (Bamberger, *B.* 17, 2421). Long yellow silky needles. V. sol. hot alcohol and HOAc.—A'_2Ba.

m-Nitro-toluene-azo-acetone [4:2:1]$C_6H_3(CH_3)(NO_2)-N_2-CH_2.CO.CH_3$.[134°]. Formed by the action of a dilute solution of aceto-acetic ether (1 mol.) and KOH (1 mol.) on a solution of nitro-diazo-toluene nitrate (from nitro-*p*-toluidine[114°]) (Bamberger, *B.* 17, 2421). Orange-red prisms. V. sol. alcohol and ether.

m-Nitro-toluene-azo-acetophenone [4:2:1]$C_6H_3(CH_3)(NO_2)-N_2-CH_2.CO.C_6H_5$. [168°]. Glistening yellow needles. Formed, together with nitro-toluene-azo-benzoyl-acetic ether, by adding a solution of nitro-diazo-toluene chloride (from *m*-nitro-*p*-toluidine [114°]) to an iced alkaline solution of benzoyl-acetic ether.

Ketoxim $C_{15}H_{13}N_2(NO_2)$:NOH:[174°]; orange needles (Bamberger a. Calman, *B.* 18, 2566).

m-Nitro-p-toluene-azo-benzoyl-acetic acid [4:2:1] $C_6H_3(CH_3)(NO_2).N_2.CH(CO.C_6H_5).CO_2H$. [194°]. Its ethyl-ether is formed, together with

m-nitro-p-toluene-azo-acetophenone, by adding a solution of *m*-nitro-*p*-diazo-toluene chloride to an iced alkaline solution of benzoyl-acetic ether (Bamberger a. Calman, *B.* 18, 2566). Silky yellow needles. V. sl. sol. cold alcohol and acetic acid, more easily at the boiling-point.

***p*-Oxy-benzene-azo-benzene-*m*-sulphonic acid** [4:1] $C_6H_4(OH)-N_2-C_6H_4.SO_3H$ [1:3]. From diazotised amido-benzene *m*-sulphonic acid and an alkaline solution of phenol. Leaflets, with violet reflex; insol. ether, v. sol. water and alcohol. –KA′: long needles (Griess, *B.* 11, 2191).

***p*-Oxy-benzene-azo-benzene-*p*-sulphonic acid** [4:1] $C_6H_4(HSO_3)-N_2-C_6H_4(OH)$ [1:4]. *Tropæoline* Y. Prepared by the action of an aqueous alkaline solution of phenol on *p*-diazobenzene sulphonic acid (Griess, *B.* 11, 2192). Yellowish red prisms. V. sol. water and alcohol.

S a l t s. — BaA″: orange pp.—BaA′$_2$ 2aq. — BaA′$_2$ 5aq: minute orange tables, sl. sol. water. —KA′: yellow rhombic leaflets, S. ·26 at 15° (Wilsing, *A.* 215, 232).

***p*-Oxy-benzene-azo-benzene sulphonic acid** [4:1] $C_6H_4(OH)-N_2-C_6H_4.SO_3H$. From azoxybenzene (1 pt.) and fuming H_2SO_4 (5 pts.) at 110° (Limpricht, *B.* 15, 1295; Wilsing, *A.* 215, 229); Tschirwinsky (*J. R.* 5, 217) considers this acid to be identical with the preceding. Small lustrous reddish plates, v. sol. water, m. sol. dilute acids or alcohol. Br does not act on the potassium salt. $SnCl_2$ forms no aniline by reduction. S a l t s.—KA′aq: S. ·85 at 15°. - BaA′$_2$.— AgA. – MgA′$_2$ 6aq.—CuA′$_2$ 6aq.

Chloride. [122°]. Orange 6- or 8-sided plates.

Amide. [212°]. Plates.

Di-oxy-benzene-azo-benzene sulphonic acid [4:2:1] $C_6H_3(OH)_2-N_2-C_6H_4.SO_3H$ [1:4]. *Tropæolin* O. *Chrysoïne.* Formed by sulphonating benzene-azo-resorcin at 100° (Witt, *C. J.* 35, 183) or from diazotised amido-benzene *p*-sulphonic acid and resorcin dissolved in KOHAq (Griess, *B.* 11, 2195). Red leaflets with steel-blue reflex; v. sl. sol. alcohol and cold water. – KA′.—BaA′$_2$ 4aq.

The absorption-spectrum has been examined by Hartley (*C. J.* 51, 182).

Di-oxy-benzene-azo-benzene *m*-sulphonic acid [4:2:1] $C_6H_3(OH)_2-N_2-C_6H_4.SO_3H$ [1:3]. From resorcin and diazotised amido-benzene *m*-sulphonic acid. Orange needles.—KA′: hygroscopic needles.

Tri-oxy-benzene-azo-benzene sulphonic acid [2:4:6:1] $C_6H_2(OH)_3-N_2-C_6H_4.SO_3H$ [1:4]. From diazotised amido-benzene *p*-sulphonic acid and an alkaline solution of phloroglucin (Stebbins, *C. N.* 42, 44; *A. C. J.* 1, 465; 2, 236; *B.* 13, 716). Yellow leaflets with green lustre. –NaA′: yellow leaflets, easily soluble in water.

***p*-Oxy-benzene-*m*-azo-benzoic acid** [4:1] $C_6H_4(OH)-N_2-C_6H_4.CO_2H$ [1:3]. [220°].

Formation.—1. From *m*-diazo-benzoic acid and phenol (Griess, *B.* 14, 2032). –2. By gently warming *m*-carboxy-diazo-benzene-*m*-carboxy-anilide $C_6H_4(CO_2H).N_2.NH.C_6H_4(CO_2H)$ with phenol, *m*-amido-benzoic acid being eliminated (Heumann a. Oeconomides, *B.* 20, 906). Red needles or plates; sol. alcohol and ether, sl. sol. water. Dyes wool and silk yellow.—BaA′$_2$ 3½aq.

Di-oxy-benzene-*m*-azo-benzoic acid [4:2:1] $C_6H_3(OH)_2-N_2-C_6H_4.CO_2H$ [1:3]. Prepared by the action of *m*-diazobenzoic acid on an alkaline solution of resorcin (Griess, *B.* 14, 2034). Brownish-red needles or brownish-yellow plates. Sol. alcohol. Dyes wool and silk yellow.

Oxy-benzene-azo-*p*-cresol. *Ethyl ether* [4:1] $C_6H_4(OEt)-N_2-C_6H_3(CH_3)(OH)$ [1:5:2] or $C_6H_3Me\!\left\langle\begin{array}{l}O\\ |\\ N_2H.C_6H_3Me(OEt)\end{array}\right.$. [104°]. Formed by combining *p*-diazo-phenetol with *p*-cresol (Liebermann a. Kostanecki, *B.* 17, 883). Golden plates. Sol. alkalis. Dissolves in H_2SO_4 with a brown colour. On reduction it gives *p*-amido-phenetol and amido-*p*-cresol.

***o*-Oxy-benzene-azo-*o*-cresol.** *Methyl ether* $C_6H_4(OMe)-N_2-C_6H_3Me(OH)$. [68°]. From diazotised *o*-anisidine and *o*-cresol (Kanonnikoff, *J. R.* 1885, 369). *Di-methyl ether* [103°].

***o*-Oxy-benzene-azo-*m*-cresol.** *Methyl ether.* [161°]. Prepared like the preceding (K.).

Di-oxy-benzene-azo-ψ-cumene [4:2:1] $C_6H_3(OH)_2-N_2-C_6H_2Me_3$ [199°]. Formed, together with the disazo-compound, by combining diazo-cumene chloride (from amido-pseudo-cumene [62°]) with resorcin (Liebermann a. Kostanecki, *B.* 17, 131, 882). Small red needles. Dissolves in alkalis with a brownish-yellow colour.

Di-oxy-benzene-azo-hydroquinone [5:2:1] $C_6H_3(OH)_2-N_2-C_6H_3(OH)_2$ [1:2:5]. *Azo-hydroquinone.* *Tetra-methyl derivative* $C_6H_3(OMe)_2.N_2.C_6H_3(OMe)_2$. [140°]. Formed by reduction of nitro-di-methyl-hydroquinone in alkaline solution (Baessler, *B.* 17, 2124; *C. C.* 1886, 671). Red needles. V. sol. alcohol, benzene, chloroform, and CS_2, v. sl. sol. water. Dissolves in strong HCl with a blue colour.

Tetra-ethyl derivative [128°]. From nitro-di-ethyl-hydroquinone, powdered zinc, and alcoholic potash (Nietzki, *B.* 12, 39).

Di-oxy-benzene-azo-naphthalene sulphonic acid [4:2:1] $C_6H_3(OH)_2-N_2-C_{10}H_6.SO_3H$ [1:4]. From diazotised (α)-naphthylamine sulphonic acid and an alkaline solution of resorcin (Stebbins, jun., *A. C. J.* 2, 36; *C. N.* 42, 44). Dark-brown needles, sol. water.

***p*-Oxy-benzene-azo-(α)-naphthylamine** [4:1] $C_6H_4(OH)-N_2-C_{10}H_6.NH_2$ [1:4]. [170°]. Prepared by the action of *p*-diazophenol nitrate on (α)-naphthylamine (Weselsky a. Benedikt, *B.* 12, 229). Orange needles (containing 3aq).— $B'_2H_2SO_4$ 6aq: green needles, insol. water.

***o*-Oxy-benzene-azo-(β)-naphthylamine** [2:1] $C_6H_4(OH).N_2C_{10}H_8$ or $C_{10}H_6\!\left\langle\begin{array}{l}NH\\ |\\ N_2H.C_6H_4OH.\end{array}\right.$

o-Oxy-benzene-hydrazimido-naphthalene. [193°]. Formed by combining *o*-diazo-phenol with (β)-naphthylamine. Slender red needles (from alcohol or acetic acid), or dark red plates (from benzene). It dissolves in aqueous or alcoholic NaOH, but is insoluble in water. By heating at 150° with HCl it is split up into (β)-naphthylamine, pyrocatechin, and nitrogen. Bromine in cold acetic acid solution gives di-bromo-(β)-naphthylamine, a brominated pyrocatechin, and nitrogen. On reduction with zinc dust and acetic acid it yields (1:2)-naphthylene-diamine.

Acetyl derivative [198°].

Benzoyl derivative [183°].

Methyl ether $C_6H_4(OMe).N_2C_{10}H_6$ [138°]; dark-red monoclinic prisms; insoluble in water (Sachs, *B.* 18, 3125).

p-Oxy-benzene-azo-(β)-naphthylamine

[4:1] $C_6H_4(OH).N_2C_{10}H_8$ or $C_{10}H_6\left\langle\begin{array}{l}NH\\ |\\ N_2H.C_6H_4OH.\end{array}\right.$

p-Oxy-benzene-hydrazimido-naphthalene. [193°]. Formed by combining *p*-diazo-phenol with (β)-naphthylamine. Flat red prisms. V. sol. benzene and acetic acid, insol. water. By heating at 150° with HCl it is split up into (β)-naphthylamine, hydroquinone, and nitrogen. Bromine in cold acetic acid solution gives di-bromo-(β)-napththylamine, a brominated hydroquinone, and nitrogen. On reduction with zinc dust and acetic acid it yields (1:2)-naphthylene-diamine (Sachs, *B.* 18, 3125).

Mono-acetyl derivative [218°].

Mono-benzoyl derivative [214°].

Oxy-benzene-azo-orcin. *Methyl ether* $C_6H_4(OMe).N_2.C_6H_2(OH)_2Me$. Hair-like needles (Stebbins, *A. C. J.* 5, 32).

o-Oxy-benzene-*o*-azo phenol

[2:1] $C_6H_4(OH)$ N_2 $C_6H_4(OH)$ [1:2]. *o-Azo-phenol.* [171°]. S. (alcohol) ·3 at 20°. Prepared by fusing *o*-nitro-phenol with KOH (Weselsky a. Benedikt, *B.* 11, 398; *A.* 196, 344). Golden leaflets; may be sublimed. Insol. water.

Reactions.—1. *Bromine* added to an ethereal solution forms a tetra-bromo-derivative. 2. *Chlorine* passed into an acetic acid solution forms a tri-chloro derivative $C_{12}H_5Cl_3(OH)_2N_2$ [235°] (Bohn a. Heumann, *B.* 17, 275).—3. *Nitric acid* forms (1, 2, 4)-di-nitro-phenol

Ethyl ether $\{C_6H_4(OEt)\}_2N_2$. [131°].

o-Nitro-phenyl-ethyl ether $C_6H_4(OEt)(NO_2)$ is dissolved in alcohol and reduced with sodium-amalgam (5 per cent.), the liquid being allowed to become hot. The product is poured into water, and the pp. extracted by strong HCl which dissolves the azo- compound. On pouring the HCl solution into water, *o* azo-phenetol is thrown down (R. Schmitt a. Möhlau, *J. pr.* 126, 202). *Properties.*—Long red prisms (from alcohol). Melts under water, but insoluble therein and not volatile with steam. It begins to boil at 240°, but suffers decomposition at the same time. *Reactions.*—1. Reduced by alcoholic ammonium sulphide to the corresponding hydrazo-compound (*q. v.*). 2. Cold fuming HNO_3 forms a nitro-, and a di-nitro-, derivative.

m-Oxy-benzene-*m*-azo-phenol *Ethyl ether* [3:1] $C_6H_4(OEt)-N_2-C_6H_4(OEt)$ [1:3]. *m-Azo-phenetol.* [91°]. Formed by reducing *m*-nitro-phenetol in alcoholic solution with sodium amalgam (M. Buchstab, *J. pr.* [2] 29, 299).

Properties.—Orange prisms (from alcohol). Sol. ether. Insol. water and (difference from *o*-compound) in conc. HCl. Reduced by H_2S and alcoholic ammonia to *m*-hydrazo-phenetol.

p-Oxy-benzene-*p*-azo-phenol

[4:1] $C_6H_4(OH)$ N_2 $C_6H_4(OH)$ [1:4]. *p-Azo-phenol.* [204°].

Formation.—1. By potash-fusion from *p*-nitroso-phenol (Jaeger, *B.* 8, 1499), *p*-nitro-phenol (Weselsky a. Benedikt, *A.* 196, 339), *p*-oxy-benzene-azo-benzene *p*-sulphonic acid, or *p*-sulpho-benzene-azo-benzene *p*-sulphonic acid (Bohn a. Heumann, *B.* 15, 3037).—2. From *p*-diazo-phenol nitrate and phenol potassium.

Properties.—Slender brown needles with blue reflex (containing aq); sl. sol. water, v. sol. alcohol. Bromine gives a tetra-bromo derivative. Nitric acid (1, 2, 4)-di-nitro-phenol. Chlorine gives tri-chloro-phenol.

Salt.—$BaC_{12}H_8N_2O_2$ 4aq.

Ethyl ether $C_6H_4(OEt)-N_2-C_6H_4(OEt)$. *p-Azo-phenetol* [160°] (S. a. M.); [158°] (A.). Formed by adding sodium-amalgam (5 p.c.) to an alcoholic solution of *p*-nitro-phenyl-ethyl ether, precipitating the product with water, boiling it with dilute HCl to remove amido-phenyl-ethyl-ether, and crystallising from alcohol (Schmitt a. Möhlau, *J. pr.* 126, 199; Hepp, *B.* 10, 1652; Andreae, *J. pr.* 129, 333). *Properties.*—Glittering golden plates. M. sol. cold alcohol, v. sol. ether and chloroform. Distils with difficulty. *Reactions.*—1. Fuming HNO_3 forms the ethyl ether of di-nitro-phenol (*q. v.*) and two isomeric tri-nitro-azoxy-phenol ethyl ethers.—2. HClAq at 130° gives EtCl and *p*-azo-phenol $N_2(C_6H_4OH)_2$, but at 150° chloro-*p*-amido-phenol is got (Schmitt, *J. pr.* [2] 19, 313).

p-Oxy-benzene-azo-diphenyl sulphonic acid [4:1] $C_6H_4(OH)-N_2-C_6H_4.C_6H_4.SO_3H$. From diazotised *p*-amido-diphenyl sulphonic acid and phenol (Carnelley a. Schlevelmann, *C. J.* 49, 380). Yellow dye.—BaA'_2: insol. cold water.

m-Di-oxy-benzene-azo-diphenyl sulphonic acid [4:2:1] $C_6H_3(OH)_2-N_2-C_6H_4.C_6H_4.SO_3H$. From diazotised *p*-amido-diphenyl sulphonic acid and resorcin (Carnelley a. Schlevelmann, *C. J.* 49, 382).—NaA'.—BaA'_2.

p-Di-oxy-benzene-azo-diphenyl sulphonic acid [5:2:1] $C_6H_3(OH)_2.N_2.C_6H_4.C_6H_4.SO_3H$. From diazotised *p*-amido-diphenyl sulphonic acid and hydroquinone (Carnelley a. Schlevelmann, *C. J.* 49, 382).

p-Oxy-benzene-azo-phloroglucin $C_6H_4(OH)-N_2-C_6H_2(OH)_3$. Two modifications appear to be formed by the action of *p*-diazo-phenol nitrate on phloroglucin (Weselsky a. Benedikt, *B.* 12, 227). (*a*) Red crystalline powder (containing 3aq), sol. alcohol. (β) Green amorphous mass, insol. alcohol.

p-Oxy-benzene-azo-resorcin. *Ethyl-ether* [4:1] $C_6H_4(OEt)-N_2-C_6H_3(OH)_2$ [1:2:4]. [167°]. Formed by the action of *p*-diazo-phenetol on resorcin (Liebermann a. Kostanecki, *B.* 17, 883). Red plates. Sol. alkalis. Dissolves in H_2SO_4 with a brownish-red colour.

Dioxy-benzene-azo-resorcin

[2:6:1] $C_6H_3(OH)_2-N_2-C_6H_3(OH)_2$ [1:2:4]. *Tetra-oxy-azo-benzene.*

Di-ethyl ether $C_6H_3(OEt)_2.N_2.C_6H_3(OH)_2$. [182°]. Formed by combination of the di-ethyl ether of *o*-diazo-resorcin $C_6H_3(OEt)_2N_2OH$ [6:2:1] with resorcin. Light reddish-yellow needles. V. sol. alcohol and ether, insol. water. Dissolves in conc. alkali with a reddish yellow colour, which becomes a splendid carmine-red on dilution (Pukall, *B.* 20, 1151).

Di-oxy-benzene-azo-resorcin

[2:4:1] $C_6H_3(OH)_2.N_2.C_6H_3(OH)_2$ [1:4:2]. *Tetra-oxy-azo-benzene.*

Di-ethyl ether

$C_6H_3(OEt)_2-N_2-C_6H_3(OH)_2$. [193°]. Formed by combination of the di-ethyl ether of *p*-diazo-resorcin $C_6H_3(OEt)_2N_2OH$ [4:2:1] with resorcin. Small brown needles or short prisms with green reflex. V. sol. alcohol, ether, and aqueous

alkalis, insol. water. Carmine-red dyestuff (Pukall, *B.* 20, 1144).

Oxy-benzene-azo-resorcin-di-sulphonic acid *Mono-methyl ether* $C_6H_4(OMe).N_2.C_6H(OH)_2(SO_3H)_2$. Yellow plates (Stebbins, *A. C. J.* 5, 55).—BaA''aq: needles.

***p*-Oxy-benzene-*p*-azo-toluene** [4:1] $C_6H_4Me-N_2-C_6H_4(OH)$ [1:4]. [151°]. Formed by gently warming *p*-diazo-toluene-*p*-toluide with phenol, *p*-toluidine being split off (Heumann a. Oeconomides, *B.* 20, 905), or by warming *p*-nitroso-toluene with *p*-toluidine acetate (Kimich, *B.* 8, 1030). Orange prisms, with blue reflex.

***m*-Di-oxy-benzene-*o*-azo-toluene** [2:1] $C_6H_4(CH_3)-N_2-C_6H_3(OH)_2$ [1:2:4]. [195°]. (W.); [178°] (F.). Formed by the action of *o*-diazo-toluene on resorcin. Brownish-red felted needles.

Acetyl derivative [75°]. Orange-yellow plates (Wallach, *B.* 15, 2825; *cf.* Fischer, *B.* 20, 1579).

***m*-Di-oxy-benzene-*p*-azo-toluene** [4:1] $C_6H_4(CH_3)-N_2-C_6H_3(OH)_2$ [1:2:4] [181°]. Prepared by the action of *p*-diazo-toluene on resorcin, or by gently warming *p*-diazo-toluene-*p*-toluide with resorcin, *p*-toluidine being split off (Heumann a. Oeconomides, *B.* 20, 906). Reddish-yellow needles: sol. alcohol, ether, and aqueous alkalis. *Acetyl derivative* [98°].

Oxy-benzene-azo-toluidine [5:2:1] $C_6H_3(CH_3)(NH_2)-N_2-C_6H_4OH$ [1:4]. [172°]. Formed by saponification of the acetyl derivative. Slender brown needles. Sol. alcohol and ether, v. sl. sol. cold water. Dissolves in aqueous acids and alkalis.

Acetyl derivative $C_6H_3(CH_3)(NHAc)-N_2-C_6H_4OH$. [253°]. Prepared by diazotising the mono-acetyl derivative of (1:2:4)-tolylene-diamine and combining it with phenol (Wallach, *B.* 15, 2826). Yellow plates. Sol. acetic acid and in aqueous alkalis, sl. sol. alcohol.

Di-oxy-benzene-azo-xylene (Wallach, *B.* 15, 25). Formed by adding diazo-xylene chloride to an alkaline solution of resorcin.

Di-oxy-benzene-azo-xylene sulphonic acid [4:2:1] $C_6H_3(OH)_2-N_2-C_6H_2Me_2SO_3H$. Prepared by the action of an alkaline solution of resorcin upon diazo-xylene sulphonic acid. Slender orange needles, sl. sol. hot water; m. sol. alcohol (Griess, *B.* 11, 2197).

Oxy-carboxy-benzene-azo-naphthalene $C_{10}H_7-N_2-C_6H_3(OH)(CO_2H)$ [1:4:3]. From naphthylamine hydrochloride (9 g.), HCl, water (500 g.), and $NaNO_2$ (3·45 g.) at 0°, the filtrate being poured into a solution of salicylic acid (6·9 g.) and NaOH (6 g.) in water (500 g.). The liquid is filtered and the sodium salt ppd. by NaCl (P. F. Frankland, *C. J.* 37, 747). *Salt.*—NaA'. S. ·07 (cold). Dyes silk pale yellow. Reduced by Sn and HCl to naphthylamine and amido-salicylic acid, $C_6H_2(NH_2)(OH)CO_2H$.

Oxy-carboxy-benzene-azo-(β)-naphthol *Mono-methyl derivative* $C_6H_3(OMe)(CO_2H)-N_2-C_{10}H_6(OH)$. Prepared by the action of diazo-anisic acid on an alkaline solution of (β)-naphthol (Griess, *B.* 14, 2039). Small red needles or plates (containing 1½ aq). Sl. sol. alcohol. A'_2Ba 4aq: red minute needles.

Oxy-carboxy-benzene-azo-(β) naphthol sulphonic acid. *Methyl derivative* $C_6H_3(OMe)(CO_2H)-N_2-C_{10}H_5(OH)(SO_3H)$. From diazo-anisic acid and (β)-naphthol sulphonic acid. Brown needles. Dyes wool scarlet. BaA''_2 8aq (Griess, *B.* 14, 2039).

Oxy-carboxy-benzene-azo-(β)-naphthol-(α)-di-sulphonic acid *Methyl derivative* $C_6H_3(OMe)(CO_2H)-N_2-C_{10}H_4(OH)(SO_3H)_2$. Prepared by the action of diazo anisic acid on an alkaline solution of (β)-naphthol-(α)-di-sulphonic acid (Griess, *B.* 14, 2040). Small dark-red needles (containing 3aq). Sol. water, and alcohol, insol. ether. Dyes a blueish shade of scarlet. $A'''HK_2$ 6aq: red crystals, sol. hot water.

Oxy-carboxy-benzene-azo-oxy-benzoic acid *Di-methyl derivative* $C_6H_3(OMe)(CO_2H)-N_2-C_6H_3(OMe)(CO_2H)$. Formed by the action of sodium-amalgam on an alkaline solution of nitro-anisic acid. Insol. water. BaA''aq (Alexejeff, *C. R.* 55, 172).

Dioxy-carboxy-methyl-phthalide-azo-dioxy-phthalide-acetic acid *Tetra-methyl derivative* $C_{24}H_{22}N_2O_{12}$ *i.e.*

$$N_2\left\{C_6H(OMe)_2\langle\begin{matrix}CH.CH_2.CO_2H\\ CO\text{---}O\end{matrix}\right\}_2$$

Azo-meconic-acetic acid. [c. 257°]. Obtained by reduction of nitro-di-methoxy-phthalide-acetic acid $C_6H(OMe)_2(NO_2)\langle\begin{matrix}CO-O\\ CH.CH_2.CO_2H\end{matrix}$ with zinc-dust and aqueous NH_3. Yellow crystals. Insol. water. Dissolves in conc. H_2SO_4 with a deep blueish-violet colour (Kleeman, *B.* 20, 880).

Tri-oxy-carboxy-toluene-azo-tri-oxy-toluic acid. *Anhydride of the tetra-methyl derivative.*

$$\overset{(6:5)}{C_6H(OMe)_2}\overset{(1)}{(CO_2H)}\langle\begin{matrix}\overset{(4)}{CH_2}.O.\overset{(4)}{CH_2}\\ \underset{(3)}{N}\text{---}\underset{(3)}{N}\end{matrix}\rangle\overset{(6:5)}{C_6H(OMe)_2}\overset{(1)}{(CO_2H)}.$$

[c. 245]. Formed by reduction of nitroso-opianic acid $C_6H(OMe)_2(NO)(CHO)(CO_2H)$ with zinc-dust and aqueous NH_3. Dissolves in alkalis with a yellow colour, in conc. H_2SO_4 with an intense purple colour. — AgA': microscopic needles (from hot water).—EtA': [101°], yellow needles, v. sol. alcohol, ether, and benzene (Kleemann, *B.* 20, 878).

(β)-Oxy-naphthalene-azo-hippuric acid $CO_2H.CH_2.NH.CO.C_6H_4-N_2-C_{10}H_6(OH)$. Prepared by the action of diazo-hippuric acid on an alkaline solution of (β)-naphthol (Griess, *B.* 14, 2040). Reddish-yellow needles. Sl. sol alcohol, v. sl. sol. water and ether.

(α)-Oxy-(α)-naphthalene-(α)-azo-naphthalene-(α)-sulphonic acid [4:1] $C_{10}H_6(OH)-N_2-C_{10}H_6.SO_3H$ [1:4]. From diazotised (α)-naphthylamine sulphonic acid and (α)-naphthol. The absorption-spectrum has been examined by Hartley (*C. J.* 51, 198).

(β)-Oxy-naphthalene-azo-naphthalene sulphonic acid $C_{10}H_6(OH)-N_2-C_{10}H_6SO_3H$. From diazotised (α)-naphthylamine sulphonic acid and (β)-naphthol (Caro; Griess, *B.* 11, 2199). Reddish-brown needles (from alcohol). Red dye.—BaA'_2. The absorption-spectrum has been examined by Hartley (*C. J.* 51, 197).

Oxy-propyl-carboxy-benzene-azo-oxy-propyl-benzoic acid $CO_2H.C_6H_3(C(OH)Me_2)-N_2-C_6H_3(C(OH)Me_2)CO_2H$. Formed by reduction of nitro-oxy-propyl-benzoic acid with sodium-amalgam and water (Widmann, *B.* 15, 2550). Yellow plates. V. sl. sol.

most ordinary solvents, sl. sol. acetic acid.—Na_2A'' 10aq: thin red rectangular tables.

Oxy-sulpho-benzene-azo-benzoic acid
[3:1] $C_6H_4(CO_2H)—N_2—C_6H_3(OH)(HSO_3)$ [1:4:3]. Prepared by the action of *m*-diazobenzoic acid on an alkaline solution of phenol-*o*-sulphonic acid (Griess, *B.* 14, 2033). Brownish-red crystals (containing ½aq). Sol. water, alcohol and ether. Yellow dye. Salts.—$A''HK$ aq: yellow plates or needles, sl. sol. cold water.—A''_2H_2Ba: small yellow needles or plates.—$A''Ba$ aq: yellow crystalline pp.

Oxy-sulpho-benzene-azo-naphthalene sulphonic acid $C_6H_3(OH)(SO_3H)—N_2—C_{10}H_6.SO_3H$. From diazotised (α)-naphthylamine sulphonic acid and phenol sulphonic acid (Stebbins, *A. C. J.* 2, 446).

Oxy-toluene-azo-toluene sulphonic acid
[4:2:1] $C_6H_3(CH_3)(SO_3H)—N_2—C_6H_3(CH_3)(OH)$ [1:5:2]. Formed by the action of *p*-diazo-toluene sulphonic acid (by diazotising *p*-toluidine-sulphonic acid) on an alkaline solution of *p*-cresol (Nölting a. Kohn, *B.* 17, 358). Reddish-brown crystals with violet reflection. V. sol. water, sl. sol. alcohol. Salts.—$A'Na$: soluble yellow plates.—A'_2Ba 4aq: small reddish-brown needles, sl. sol. hot water.

Diphenyl-azo-diphenyl
$C_6H_5.C_6H_4—N_2—C_6H_4.C_6H_5$. [250°]. Orange-red plates. Sol. ether, insol. water, alcohol, and acetic acid. Formed by reduction of *p*-nitro-diphenyl with sodium-amalgam, and by the dry distillation of hydrazo-diphenyl. Prepared by oxidising an alcoholic solution of hydrazo-diphenyl with Fe_2Cl_6 (Zimmermann, *B.* 13, 1962).

Phenyl-acetic-azo-phenyl-acetic acid *v. exo*-CARBOXY-TOLUENE-AZO-PHENYL-ACETIC ACID.

Phenyl-amido-benzene-azo-benzene-sulphonic acid
[4:1] $C_6H_4(SO_3H)—N_2—C_6H_4NHPh$ [1:4]. *Tropæoline O.O.* Prepared by the action of *p*-diazobenzene sulphonic acid on an alcoholic solution of diphenylamine (Witt, *C. J.* 35, 187; *B.* 13, 262). Steel-blue hair-like needles. Sl. sol. water. Salts.—$A'K$: flat yellow needles; sl. sol. cold water.—$A'Na$.—$A'NH_4$.—$A'NHMe_3$: large yellow leaflets.—A'_2Ba and A'_2Ca: insoluble yellow pps.

Phenyl-glycollic-*o*-azo-phenyl glycollic acid
$N_2(C_6H_4.O.CH_2.CO_2H)_2$. [162°].

Preparation. — *o*-Nitrophenylglycollic acid (18·6 g.) water (140 g.) and Na_2CO_3 (5 g.) are treated at 60° with sodium-amalgam (215 g. of 4 p.c. amalgam). The crystals which separate on cooling are dissolved in very little water and the acid is ppd. by acetic acid. The product is recrystallised several times from alcohol (A. Thate, *J. pr.* [2] 29, 161).

Properties.—Orange silky needles, containing 2aq (from water or dilute alcohol). When dry (at 110°) it is brick-red. Sol. ether, alkalis and strong acids. Its solutions are yellow or red.

Reactions.—1. Aqueous solution is acid to litmus and gives with $AgNO_3$ a red gelatinous pp., and with $Pb(OAc)_2$ a flocculent yellow pp.—2. Reduced by alcoholic NH_3 and H_2S to the corresponding hydrazo- compound, the potassium salt of which, $N_2H_2(C_6H_4.O.CH_2.CO_2K)_2$ 3aq, crystallises from alcohol in rhombohedra.

Salts.—K_2A'' 3aq. Orange plates. Its solution gives with $BaCl_2$ a red crystalline pp.; with $Pb(OAc)_2$ an orange flocculent pp.; with $AgNO_3$, a red flocculent pp.; with Fe_2Cl_6 an orange pp.; with $CuSO_4$, a brownish-yellow pp.; with $HgCl_2$, on boiling, a red pp.; with $MgSO_4$ after some time, an orange crystalline pp.—Na_2A'' 3aq.—Ag_2A'' 3aq.—BaA'' 2aq.—CaA'' 8aq.

Ethyl ether. Et_2A''. [111°]. Red crystals.

Phenyl-glyoxylic-azo-phenyl-glyoxylic acid
$CO_2H.CO.C_6H_4—N_2—C_6H_4.CO.CO_2H$. *Azo-benzoyl-formic acid.* Orange needles (containing 2aq and melting at [135°]. When dry it melts at about 151°. Prepared by reduction of *m*-nitro-benzoyl-formic acid with $FeSO_4$ and KOH; yield, 50 p.c. (Thompson, *B.* 16, 1308). Sl. sol. ether and cold water, insol. acidulated water, chloroform, or benzene. Very stable body. A cold saturated aqueous solution of the acid gives with $BaCl_2$ or $CaCl_2$ a micro-crystalline pp., with $AgNO_3$ a yellow flocculent precipitate.—$A''Ba$: orange crystalline pp., insol. water.—$A''Ag_2$: orange-yellow slightly soluble pp.

Phenyl-pyrrol-azo-benzene
$C_6H_5.N_2.C_4H_3NPh$ probably $\begin{array}{l} C_6H_5.N_2.C = CH \\ \quad\quad\quad\;\; NPh| \\ \quad\quad\quad\;\; HC = CH \end{array}$.
[117°]. Prepared by adding diazobenzene chloride (1 mol.) to phenyl-pyrrol (1 mol.) dissolved in alcohol containing AcONa. Brown prisms or long reddish-yellow needles with blueish reflection. V. sol. alcohol. Dissolves in conc. H_2SO_4 with a reddish-violet colour, in alcoholic HCl with a blood-red colour. Reduced by zinc-dust and NH_3 or NaOH to aniline and (probably) amido-phenyl-pyrrol (O. Fischer a. Hepp, *B.* 19, 2256).

Di-propyl-amido-benzene-azo-di-propyl-aniline $C_6H_4N(C_3H_7)_2—N_2—C_6H_4N(C_3H_7)_2$. *Di-propyl-aniline-azyline.* [90°]. Formed by passing NO through an alcoholic solution of di-propyl-aniline (Lippmann a. Fleissner, *B.* 15, 2140; 16, 1417). Large trimetric crystals, $a:b:c:$ = 1:·629:·913. Picrate $B''(C_6H_2(NO_2)_3OH)_2$: orange-red insoluble crystals. — Periodide B''_4I_6: violet glistening needles.

Pyrrol-azo-benzene $C_6H_5—N_2—C_4H_3NH$ probably $\begin{array}{l} C_6H_5.N_2.C = CH \\ \quad\quad\quad\;\; NH| \\ \quad\quad\quad\;\; HC = CH \end{array}$. [62°]. Prepared by adding the calculated quantity of a moderately conc. solution of diazo-benzene chloride to a well-cooled solution of pyrrol (2 pts.) in alcohol (100 pts.) with addition of sodium acetate (5 pts.) (Fischer a. Hepp, *B.* 19, 2251). Yellow needles. V. sol. alcohol, ether, and petroleum spirit, sl. sol. water. It has basic properties. Easily reduced (*e.g.*, by zinc-dust and alkalis) to aniline and (probably) amido-pyrrol. Readily combines in alkaline or neutral solution with a further quantity of diazo-compound, giving disazo-bodies. Dissolves easily in dilute HCl with a reddish-yellow colour. Dissolves in conc. H_2SO_4 with a yellow colour. The platino-chloride forms small red sparingly soluble needles.

Pyrrol-*p*-azo-di-methyl-aniline
$C_6H_4(NMe_2)—N_2—C_4H_3NH$. [159°]. Formed by combining *p*-diazo-di-methyl-amido-benzene with pyrrol in dilute alkaline solution. Glittering green plates. Dissolves in very dilute HCl with a grass-green colour, in conc. HCl with a greenish-yellow colour. $PtCl_4$ gives a dark green amorphous pp. (Fischer a. Hepp, *B.* 19, 2257).

Pyrrol-(α)-azo-naphthalene $C_{10}H_7.N_2.C_4H_3NH$

$$\begin{array}{l} C_{10}H_7.N_2.C = CH \\ NH \mid \\ HC = CH \end{array}$$

probably . [103°]. Formed by adding (α)-diazo-naphthalene chloride (1 mol.) to pyrrol (1 mol.) dissolved in alcohol containing sodium acetate. Reddish-yellow plates. V. sol. alcohol (O. Fischer a. Hepp, *B.* 19, 2255).

Pyrrol-(β)-azo-naphthalene

$C_{10}H_7—N_2—C_4H_3NH$ probably

$$\begin{array}{l} C_{10}H_7.N_2.C = CH \\ NH \mid \\ HC = CH \end{array}$$

[101°]. Prepared by adding (β)-diazo-naphthalene chloride to an alcoholic solution of pyrrol containing sodium acetate. Gold-bronzy plates (O. Fischer a. Hepp, *B.* 19, 2255).

Pyrrol-*p*-azo-toluene $C_6H_4Me—N_2—C_4H_3NH$

$$\begin{array}{l} C_7H_7.N_2.C = CH \\ NH \mid \\ HC = CH \end{array}$$

probably . [82°]. Prepared by adding *p*-diazo-toluene chloride (1 mol.) to pyrrol (1 mol.) dissolved in alcohol containing sodium acetate (Fischer a. Hepp, *B.* 19, 2254).

***m*-Sulphi-benzene-azo-benzene-*m*-sulphinic acid** $C_6H_4(SO_2H)—N_2—C_6H_4(SO_2H)$. *Azo-benzene di-sulphinic acid.* Obtained from $C_6H_4(SO_2SH).N_2.C_6H_4(SO_2SH)$ by treatment with sodium amalgam (Limpricht, *B.* 18, 1473; Bauer, *A.* 229, 363). Yellowish amorphous mass, sl. sol. cold water, insol. ether.

Salts.—Na_2A'' *x*aq.—CaA'' 1½aq.—BaA''.—PbA''. These salts are readily oxidised (*e.g.* by $KMnO_4$ or I in KI) to the corresponding di-sulphonates. Conc. ammonic sulphide converts them into the di-thio-di-sulphonates. They are not reduced by sodium amalgam. Boiled with HCl the acid clots together, but conc. HCl. at 110° forms (2 p.c. of) an *isomeric base.*

***p*-Sulphi-benzene-azo-benzene-*p*-sulphinic acid** $SO_2H.C_6H_4—N_2—C_6H_4.SO_2H$. *Azo-benzene p-di-sulphinic acid.* Prepared from $SO_2Cl.C_6H_4—N_2—C_6H_4.SO_2Cl$ and $Ba(SH)_2$, or from $NaS.SO_2.C_6H_4.N_2.C_6H_4.SO_2.SNa$ by sodium amalgam (Limpricht, *B.* 18, 1475; Bauer, *A.* 229, 369). The free acid is ppd. by HCl from its salts as a bulky yellow mass, sparingly soluble in water or alcohol. Clots together when heated with acids. Salts.—Na_2A'' 4aq.—BaA''.

Sulpho-benzene-azo-amido-ethane *v.* Sulpho-benzene-azo-ethylamine.

***p*-Sulpho-benzene-azo-di-amido-benzoic acid** [4:1]$C_6H_4(SO_3H)—N_2—C_6H_2(NH_2)_2CO_2H$[1:4:2:6]. Formed by the action of *p*-diazo-benzene-sulphonic acid on *s*-di-amido-benzoic acid (Griess, *B.* 15, 2199). Needles or plates. Sl. sol. water, cold alcohol, and ether. Very unstable. Decomposes by boiling with water. On reduction it gives sulphanilic acid and (5:3:2:1)-tri-amido-benzoic acid.

Sulpho-benzene-azo-aniline-sulphonic acid [4:1] $C_6H_4(HSO_3)—N_2—C_6H_3(HSO_3)NH_2$ [1:?:4]. *Amido-azo-benzene disulphonic acid.* Formed by sulphonation of *p*-amido-benzene-azo-benzene-*p*-sulphonic acid (Griess, *B.* 15, 2187). Violet glistening needles. Sol. hot water. Dyes silk and wool yellow. On reduction with tin and HCl it gives sulphanilic acid and *p*-phenylene-diamine-sulphonic acid. BaA'' 7½aq: orange needles, sol. hot water.

***m*-Sulpho-benzene-azo-benzene-*m*-sulphonic acid** [3:1] $SO_3H.C_6H_4—N_2—C_6H_4.SO_3H$ [1:3].

Formation.—1. From nitro-benzene *m*-sulphonic acid by treatment with sodium-amalgam (Claus a. Moser, *B.* 11, 762) or, better, with powdered zinc and KOH (Mahrenholtz a. Gilbert, *A.* 202, 332).—2. One of the acids got by sulphonating benzene-azo-benzene at 150° (Janovsky, *M.* 3, 244).—3. From potassium *m*-amido-benzene sulphonate and $KMnO_4$.

Monoclinic prisms, sl. sol. water and alcohol, insol. ether.

Salts.—Na_2A'' 3½aq.: monoclinic crystals.—$(NH_4)_2A''$ 2aq. — CaA'' 4aq. — BaA'' 5aq. — PbA'' 4½aq.

Amide [290°]. Prisms, sl. sol. water.

Ethyl ether Et_2A''. [100°].

Chloride $C_6H_4(SO_2Cl).N_2.C_6H_4(SO_2Cl)$. [166°]. Acts upon cold conc. aqueous $Ba(SH)_2$ thus: $C_6H_4(SO_2Cl).N_2.C_6H_4(SO_2Cl) + 2BaH_2S_2 = N_2(C_6H_4.SO_2.S)_2Ba + BaCl_2 + 2H_2S$ forming thio-sulpho-benzene-azo-benzene-thio-sulphonic acid, part of which then decomposes according to the following equation: $N_2(C_6H_4.SO_2.S)_2Ba + H_2S = H_2N_2(C_6H_4.SO_2.S)_2Ba + S$ forming the barium salt of hydrazobenzene di-thio-di-sulphonic acid (Bauer, *A.* 229, 353).

***m*-Sulpho-benzene-azo-benzene-*p*-sulphonic acid** [4:1] $C_6H_4(HSO_3)—N_2—C_6H_4(HSO_3)$ [1:3]. Formed, together with the *p*-*p*-acid, by heating benzene-azo-benzene with H_2SO_4 at 160° (Limpricht, *B.* 14, 1356; Rodatz, *A.* 215, 216), and by the oxidation of a mixture of *m*- and *p*-potassium amido-benzene sulphonate with $KMnO_4$. Uncrystallised syrup. On heating with dilute HCl to 150° it gives *p*- and *m*-amido-benzene-sulphonic acids (Limpricht, *B.* 15, 1155).

Salts.—K_2A'' 2½aq: yellow needles, v. sol. water.—Ag_2A''.

Chloride [125°]: red needles.

Amide [258°]: slender yellow needles.

***p*-sulpho-benzene-azo-benzene-*p*-sulphonic acid.** [4:1] $SO_3H.C_6H_4—N_2—C_6H_4.SO_3H$ [1:4].

Formation.—1. By oxidising amido-benzene-*p*-sulphonic acid with $KMnO_4$ (Laar, *B.* 14, 1928; Limpricht, *B.* 18, 1414).—2. Among the products of the sulphonation of benzene-azo-benzene at 160° (Limpricht, *B.* 14, 1356; 15, 1155; Janovsky, *M.* 3, 242).

Properties.—Ruby-red needles containing 2 or 3 aq (J.), or aq (L.). Melts at about 60° or, when dry, at about 150°. HClAq at 150° gives sulphanilic acid and other products.

Salts: K_2A'' 2½aq: sl. sol. water.—Na_2A''.—$(NH_4)_2A''$.—Ag_2A''.—CaA''.—PbA''aq.—CuA''6aq.

Chloride [222°]. Red needles.

Amide [above 300°]; orange plates or needles, sl. sol. hot water.

Di-sulpho-benzene-azo-benzene-disulphonic acid [5:3:1] $C_6H_3(SO_3H)_2.N_2.C_6H_3(SO_3H)_2$ [1:3:5]. From nitro-benzene-di-sulphonic acid, zinc dust, and baryta (Reiche, *A.* 203, 64). Very deliquescent crystals.—K_4A^{iv} 3aq.—Ba_2A^{iv} 5aq.

Di-sulpho-benzene-azo-benzene-di-sulphonic acid [4:3:1] $C_6H_3(SO_3H)_2.N_2.C_6H_3(SO_3H)_2$ [1:3:4]. From the corresponding nitro-benzene di-sulphonic acid, zinc dust, and baryta-water (Reiche, *A.* 203, 70). Salts.—K_4A^{iv} 3aq.—Ba_2A^{iv} 4aq.

Chloride [58°]; radiating needles.

Amide [222°]; white needles.

***p*-Sulpho-benzene-azo-*o*-cresol.** [4:1] $C_6H_4(SO_3H)—N_2—C_6H_3(CH_3)(OH)$ [1:3:4].

Formed by the action of diazo-benzene-*p*-sulphonic acid (by diazotising sulphanilic acid) on an alkaline solution of *o*-cresol (Nölting a. Kohn, *B.* 17, 364). Small reddish-brown needles. Sol. hot water. V. sl. sol. alcohol. On reduction with tin and HCl it gives sulphanilic acid and amido-*o*-cresol $C_6H_2(CH_3)(NH_2)(OH)$ [1:5:2].

Salts.—$A'Na$ 2aq: yellow soluble plates. A'_2Ba 3aq: yellow tables, sl. sol. hot water.

***p*-Sulpho-benzene-azo-*m*-cresol** [4:1] $C_6H_4(SO_3H)-N_2-C_6H_3(CH_3)(OH)$ [1:2:4]. Formed by the action of diazobenzene-*p*-sulphonic acid on an alkaline solution of *m*-cresol (Nölting a. Kohn, *B.* 17, 366). Small reddish-brown crystals with violet reflex. V. sol. water and hot alcohol. Orange-yellow dye stuff. On reduction it gives sulphanilic acid and amido-*m*-cresol $C_6H_3(CH_3)(NH_2)(OH)$ [1:2:5].

Salts: $A'Na$: small yellow soluble needles. A'_2Ba: yellow plates, v. sl. sol. cold water.

Sulpho-benzene-azo-*p*-cresol [4:1] $C_6H_4(SO_3H)-N_2-C_6H_3(CH_3)(OH)$ [1:5:2].

or
$$\begin{array}{l} \quad\quad\quad\quad O \\ \quad\quad\quad\quad | \rangle C_6H_3CH_3. \\ C_6H_4(SO_3H)-N_2H \end{array}$$

Formation.—1. By the action of *p*-diazobenzene-sulphonic acid on an alkaline solution of *p*-cresol.—2. By sulphonation of benzene-azo-*p*-cresol (Nölting a. Kohn, *B.* 17, 355). Yellowish-brown plates with violet reflex. V. sol. water and hot alcohol. Dyes silk and wool orange-yellow. On reduction with tin and HCl it yields sulphanilic acid and amido-*p*-cresol $C_6H_2(CH_3)(NH_2)(OH)$ [1:3:4].

Salts: $A'Na$: soluble yellow plates. $A'K$ 3aq.—A'_2Mg 5aq.—A'_2Ba: yellowish-brown tables, sl. sol. hot water.

***p*-Sulpho-benzene-azo-ψ-cumenol** [4:1] $C_6H_4(HSO_3)-N_2-C_6H(CH_3)_3OH$ [1:3:5:6:2]. Formed by combining diazo-benzene-*p*-sulphonic acid with ψ-cumenol [70°]. $-KA'$ 2aq: orange needles (Liebermann a. Kostanecki, *B.* 17, 887).

Sulpho-benzene-azo-ethylamine. Potassium salt. $C_6H_4(SO_3K)-N_2-CH(NH_2).CH_3$. From the potassium salt of the corresponding nitro-compound by reducing with ammonium sulphide (Kappeler, *B.* 12, 2285). Silvery plates (from water); sl. sol. water, insol. Na_2CO_3Aq. NaOHAq dissolves it with crimson colour.

***m*-Sulpho-benzene-azo-(α)-naphthol** [3:1] $C_6H_4(HSO_3)-N_2-C_{10}H_6.OH$ [1:4]. Prepared by the action of an alkaline solution of (α)-naphthol on *m*-diazobenzene sulphonic acid (Griess, *B.* 11, 2197). Small greenish leaflets. Sl. sol. cold water and cold alcohol.

***m*-Sulpho-benzene-azo-(β)-naphthol** [3:1] $C_6H_4(HSO_3)-N_2-C_{10}H_6(OH)$ [1:2] or
$$\begin{array}{l} \quad\quad\quad\quad\quad O \\ \quad\quad\quad\quad\quad | \rangle C_{10}H_6. \\ C_6H_4(HSO_3)-HN_2 \end{array}$$
Prepared by the action of an alkaline solution of (β)-naphthol on *m*-diazobenzene sulphonic acid (Griess, *B.* 11, 2197). Slender red needles. V. sol. alcohol and water. BaA'_2 5aq: yellowish-red scales. Sl. sol. water.

***p*-Sulpho-benzene-azo-(α)-naphthol** [4:1] $C_6H_4(SO_3H)-N_2-C_{10}H_6(OH)$ [1:4]. *Tropæoline OOO*, No. 1. From *p*-diazobenzene sulphonic acid and an alkaline solution of (α)-naphthol (Liebermann a. Jacobsen, *A.* 211, 61). Orange-dye. Its absorption spectrum is given by Hartley (*C. J.* 51, 184).

***p*-Sulpho-benzene-azo-(β)-naphthol** [4:1] $C_6H_4(SO_3H)-N_2-C_{10}H_6(OH)$ [1:2] or
$$\begin{array}{l} \quad\quad\quad\quad O \\ \quad\quad\quad\quad | \rangle C_{10}H_6. \\ C_6H_4(SO_3H)-HN_2 \end{array}$$
Tropæoline OOO No. 2. From *p*-diazo-benzene sulphonic acid and (β-) naphthol (W. v. Miller, *B.* 13, 268; Hofmann, *B.* 10, 1378; Griess, *B.* 11, 2198). The absorption spectrum has been examined by Hartley (*C. J.* 51, 185).

***p*-Sulpho-benzene-azo-(β)-naphthol sulphonic acid** [4:1] $C_6H_4(HSO_3)-N_2-C_{10}H_5(HSO_3)OH$. Prepared by the action of *p*-diazobenzene sulphonic acid on an alkaline solution of (β)-naphthol sulphonic acid (Griess, *B.* 11, 2198; Stebbins, *A. C. J.* 2, 236). Yellowish red crystals. Excessively soluble in water. BaA'' 7½aq: difficultly soluble orange microscopic needles.

***p*-Sulpho-benzene-azo-(α)-naphthylamine** [4:1] $C_6H_4(HSO_3)-N_2-C_{10}H_6.NH_2$ [1:4]. From diazotised sulphanilic acid and (α)-naphthylamine (Griess, *B.* 12, 427). Brownish-violet needles, v. sl. sol. boiling water. Its acid solutions have a deep magenta colour (Griess's test for nitrous acid); its alkaline solutions are orange. On reduction with tin and HCl it gives sulphanilic acid and (1, 4)-naphthylene-diamine.

Salts: KA' 3aq: brownish-yellow plates, sol. hot water.—BaA'_2 3aq: sparingly soluble brown needles (Griess, *B.* 15, 2190).

***p*-Sulpho-benzene-azo-(β)-naphthylamine** [4:1] $C_6H_4(HSO_3)-N_2-C_{10}H_6.NH_2$ [1:2] or
$$\begin{array}{l} \quad\quad\quad\quad HN \\ \quad\quad\quad\quad | \rangle C_{10}H_6. \\ C_6H_4(HSO_3)-HN_2 \end{array}$$
Formed by the action of *p*-diazo-benzene-sulphonic acid on (β)-naphthylamine hydrochloride (Griess, *B.* 15, 2191). Small yellowish-red needles. Sl. sol. water, v. sol. hot alcohol, insol. ether. On reduction with tin and HCl it gives sulphanilic acid and (1, 2)-naphthylene-diamine.—KA' 7½aq: orange plates, sol. hot water.

Sulpho-benzene-azo-(α)-naphthylamine sulphonic acid $C_6H_4(SO_3H).N_2.C_{10}H_5(SO_3H).NH_2$ [1:4:2]. Formed by the action of *p*-diazo-benzene-sulphonic acid on (α)-naphthylamine-sulphonic acid (Griess, *B.* 15, 2194). Needles or plates. Sol. water and alcohol, insol. ether, dyes silk and wool orange.—BaA'' 7½aq: red needles or plates, sol. hot water.—$BaH_2A''_2$ 8aq: sparingly soluble violet-brown needles.

***p*-Sulpho-benzene-azo-(β)-naphthyl-phenyl-amine** $C_6H_4(SO_3H)-N_2-C_{10}H_6.NHC_6H_5$ or
$$\begin{array}{l} C_6H_4(SO_3H).HN_2.C_{10}H_6 \\ \quad\quad\quad\quad \diagdown\diagup \\ \quad\quad\quad\quad N.C_6H_5 \end{array}$$
Prepared by slowly adding dry *p*-diazobenzene-sulphonic acid (18 g.) to a solution of phenyl-(β)-naphthylamine (22 g.) in glacial acetic acid (100 c.c.) at c. 50°, followed by finely powdered dry K_2CO_3 (7 g.); the compound separates out in glistening red needles of the potassium-salt. It is a splendid scarlet dyestuff, but is very fugitive in light. The potassium salt is easily soluble in water; when cold its solution solidifies to a transparent red jelly. HCl precipitates the free acid. By $SnCl_2$ it is reduced to phenyl-*o*-naphthylene-diamine and sulphanilic acid. By boiling with dilute

mineral acids it is converted into naphthophenazine and sulphanilic acid:

$$C_6H_4(SO_3H).N_2.C_{10}H_6.NHC_6H_5 =$$

$C_{10}H_6<{}^{N}_{N}>C_6H_4 + C_6H_4(NH_2)SO_3H$. The Ba and Ca salts are crystalline insoluble pps. (Witt, *B.* 20, 572).

***p*-Sulpho-benzene-azo-nitro-isobutane** $C_6H_4(HSO_3)-N_2-C_4H_8(NO_2)$. Prepared by the action of *p*-diazobenzene-sulphonic acid on an alkaline solution of nitro-iso-butane.—KA′aq: orange-yellow needles. Soluble in alkalis to a red solution. Dyes silk orange (Kappeler, *B.* 12, 2288).

***p*-Sulpho-benzene-azo-nitro-ethane** $C_6H_4(HSO_3)-N_2-C_2H_4(NO_2)$. Prepared by the action of *p*-diazobenzene-sulphonic acid on an alkaline solution of nitro-ethane. A′K: golden yellow leaflets, sparingly soluble in cold water, soluble in alkalis to a blood-red solution (Kappeler, *B.* 12, 2286).

***p*-Sulpho-benzene-azo-nitro-methane** $C_6H_4(HSO_3)-N_2-CH_2(NO_2)$. Prepared by the action of *p*-diazobenzene-sulphonic acid on an alkaline solution of nitro-methane. KA′3aq: orange needles. Dyes silk orange (Kappeler, *B.* 12, 2286).

***p*-Sulpho-benzene-azo-nitro-propane** $C_6H_4(HSO_3)-N_2-C(NO_2)(CH_3)_2$. Prepared by the action of *p*-diazobenzene-sulphonic acid on an alkaline solution of nitro-isopropane. A′K: light-yellow leaflets. Has no dyeing power. Insoluble in alkalis (Kappeler, *B.* 12, 2287).

***p*-Sulphobenzene-azo-orcin** [4:1] $C_6H_4(HSO_3)-N_2-C_6H_2(CH_3)(OH)_2$. Small yellowish-red needles. Difficultly soluble in water. Prepared by the action of an alkaline solution of orcin upon *p*-diazobenzene-sulphonic acid.—KA′2aq (Griess, *B.* 11, 2196).

***p*-Sulpho-benzene-azo-*o*-oxy-benzoic acid** [4:1] $C_6H_4(SO_3H)-N_2-C_6H_3(OH)(CO_2H)$ [1:4:5]. From diazotised sulphanilic acid and an alkaline solution of salicylic acid. Golden needles; sl. sol. hot water (Griess, *B.* 11, 2196; Stebbins, *B.* 13, 716). $BaH_2A''_2$.

***p*-Sulpho-benzene-azo-oxy-quinoline** $C_6H_4(HSO_3)-N_2-\overset{(B.1)}{C_6H_2}\overset{(B.4)}{(OH)}<{}^{CH:CH}_{N\,:\,CH}$. Formed by the combination of *p*-diazo-benzene-sulphonic acid with (*B.*4)-oxy-quinoline (Fischer a. Renouf, *B.* 17, 1642). Small needles. Orange dye.

***p*-Sulpho-benzene-azo-phenol disulphonic acid** $C_6H_4(SO_3H)-N_2-C_6H_2(SO_3H)_2(OH)$. Formed by heating azoxybenzene with fuming H_2SO_4. Small soluble flat red needles with green lustre. On reduction it gives *p* amido-benzene-sulphonic acid and amido-phenol-di-sulphonic acid.

Salts.—$A'''K_3$3aq: yellow microscopic needles, easily soluble. Bromine-water gives tri-bromo-phenol.—A′′′Ag: unstable red pp.—$A'''_2Ba_3$7aq: brown crystalline pp.—$A'''_2Pb_3$1½aq.

Chloride: red crystalline powder [220°].

Amide: yellow plates [260°], sparingly soluble in alcohol (Limpricht, *B.* 15, 1297; Wilsing, *A.* 215, 234).

***p*-Sulpho-benzene-azo-xylenol** [4:1] $C_6H_4(SO_3H)-N_2-C_6H_2Me_2.OH$ [1:3:5.2]. Formed by combining diazobenzene-*p*-sulphonic acid with *m*-xylenol $C_6H_3Me_2(OH)$ [1:3:4] (Grevingk, *B.* 19, 148). Dyes wool and silk a brownish yellow from an acid bath. On reduction it yields sulphanilic acid and *o*-amido-*m*-xylenol $C_6H_2Me_2(NH_2)(OH)$ [5:3:1:2].

Sulpho - carboxy - benzene - azo - (β) - naphthol-(α)-di-sulphonic acid $C_6H_3(CO_2H)(SO_3H)-N_2-C_{10}H_4(OH)(SO_3H)_2$. Prepared by the action of *m*-diazo-sulpho-benzoic acid on an alkaline solution of (β)-naphthol-(α)-di-sulphonic acid (Griess, *B.* 14, 2038). Orange needles or prisms. V. sol. water and alcohol, insol. ether. Salts.—$A^{iv}_2H_2Ba_3$3aq: slightly soluble yellow needles. $A^{iv}Ba_2$5aq: nearly insoluble red crystalline pp.

Sulpho-carboxy-benzene-azo-oxy-naphthoic acid $C_6H_3(SO_3H)(CO_2H)-N_2-C_{10}H_5(OH)(CO_2H)$. Prepared by the action of diazosulphobenzoic acid on an alkaline solution of (α)-oxy-naphthoic acid (Griess, *B.* 11, 2199). Brown microscopic needles or leaflets. Sl. sol. water.

Sulpho-naphthalene-azo-(β)-naphthol-disulphonic acid $C_{10}H_6(SO_3H).N_2.C_{10}H_4(OH)(SO_3H)_2$. Crimson dye (Stebbins, *A. C. J.* 2, 446).

Sulpho-toluene-azo-toluene-sulphonic acid [2:4:1] $C_6H_3Me(SO_3H).N_2.C_6H_3Me(SO_3H)$ [1:2:4]. From potassium *o*-toluidine sulphonate (of Gerver) and $KMnO_4$ (Kornatzki, *A.* 221, 183). Small red prisms, grouped in tables, very soluble in water and in alcohol. K_2A'': red plates grouped in clumps.—BaA″aq.—CaA″3aq. PbA″aq.

Chloride. [218°]. Red needles (from C_6H_6).

Amide. [250°]. Tables (from aqueous NH_3).

Sulpho-toluene-azo-toluene-sulphonic acid [2:5:1] $C_6H_3Me(SO_3H).N_2.C_6H_3Me(SO_3H)$ [1:2:5]. *Azo-toluene-disulphonic acid.* From *o*-nitro-toluene sulphonic acid, zinc dust, and KOHAq (Neale, *A.* 203, 74); or from *o*-toluidine sulphonic acid of Hayduck and $KMnO_4$ (Kornatzki, *A.* 221, 181). Salts.—BaA″4aq.—K_2A''2½aq.—CaA″5aq.—PbA″4aq.

Chloride. [220°]. Red prisms.

Amide. [300°]. Red powder.

Sulpho-toluene-azo-toluene-sulphonic acid [4:6:1] $C_6H_3Me(SO_3H).N_2.C_6H_3Me(SO_3H)$ [1:4:6]. From potassium *p*-toluidine sulphonate and $KMnO_4$ (Kornatzki, *A.* 221, 182).

Salt.—BaA″3aq.

Sulpho-toluene-azo-toluene-sulphonic acid [4:5:1] $C_6H_3Me(SO_3H).N_2.C_6H_3Me(SO_3H)$ [1:4:5]. From *p*-nitro-toluene *o*-sulphonic acid, KOHAq, and zinc dust (Neale, *A.* 203, 80); or from potassic *p*-toluidine sulphonate and $KMnO_4$.

K_2A''3aq.—CaA″3aq.—BaA″aq.—PbA″2aq.

Chloride. [194°]. Red crystals.

Amide. [270°]. Yellow.

Exo-**Sulpho-toluene-azo-toluene-*exo*-sulphonic acid** $SO_3H.CH_2.C_6H_4.N_2.C_6H_4.CH_2.SO_3H$.

Formation.—1. From $C_6H_4(NO_2).CH_2.SO_3H$ by boiling with zinc dust and KOH or $Ba(OH)_2$.—2. From $C_6H_4(NH_2).CH_2.SO_3K$ and $KMnO_4$ (Mohr, *A.* 221, 223). Salts.—K_2A''½aq: orange plates.—BaA″1½aq.—Ag_2A''aq.

Chloride. [149°].

Sulpho-xylene-azo-di-bromo-naphthol $C_6H_2Me_2(SO_3H)-N_2-C_{10}H_4Br_2(OH)$. From *p*-diazo-xylene sulphonic acid and di-bromo-(α)-naphthol (Stebbins, jun., *A. C. J.* 2, 446). Sol. hot water, forming a scarlet solution.

Sulpho-xylene-azo-(α)-naphthol $C_6H_2Me_2(SO_3H)-N_2-C_{10}H_6OH$. From *p*-diazo-

xylene sulphonic acid and (α)-naphthol (Stebbins, jun., *A. C. J.* 2, 446). Brown dye; sol. water.

Sulpho-*m*-xylene-azo-(β)-naphthol [1:3:6:4] $C_6H_2Me_2(SO_3H)—N_2—C_{10}H_6(OH)$. Formed by the action of diazo-*m*-xylene sulphonic acid (from *m*-xylidine sulphonic acid) upon an alkaline solution of (β)-naphthol (Nölting a. Kohn, *B.* 19, 139). Metallic green crystals. Sl. sol. cold water. Dyes wool and silk from an acid bath a yellowish shade of scarlet.

Salts.—A'Na^x: red soluble plates.—A'_2Ba: sl. sol. hot water.

Sulpho-xylene-azo-(β)-phenanthrol. From *p*-diazo-xylene sulphonic acid and (β)-phenanthrol (Stebbins, *A. C. J.* 2, 446). Reddish-brown dye.

Sulpho-xylene-azo-resorcin *v.* DI-OXY-BENZENE-AZO-XYLENE SULPHONIC ACID.

Sulpho-xylene-azo-xylene sulphonic acid [2:4:5:1] $C_6H_2Me_2(SO_3H)—N_2—C_6H_2Me_2(SO_3H)$ [1:2:4:5]. Formed by oxidising (1, 3, 6, 4)-xylidine sulphonic acid with dilute $KMnO_4$ (Jacobsen a. Ledderboge, *B.* 16, 194); or by reducing (6, 1, 3, 4)-nitro-xylene sulphonic acid with zinc-dust and NaOH (Limpricht, *B.* 18, 2191). Orange plates; v. sol. water; sl. sol. acids.

Salts.—K_2A''4aq.—KHA''4aq.

Chloride. [86°]; red crystals.

Amide. [174°].

***m*-Thio-sulpho-benzene-azo-benzene-sulphinic acid** [3:1] $(HS.SO_2)C_6H_4.N_2.C_6H_4(SO_2H)$ [1:3]. [below 100°]. A solution of the barium thio-sulpho-benzene-azo- (or hydrazo-) benzene-thio-sulphonate gives, on evaporation, S and the salt of the present acid. This salt forms red crusts which are sparingly soluble in water, but are converted by boiling Na_2CO_3 into the soluble Na salt, whence HCl separates the free acid as a bulky flocculent pp. hardly soluble in water, but resinified by boiling with it. It is soluble in alcohol. Oxidised by $KMnO_4$ to $N_2(C_6H_4SO_3K)_2$.

Salts.—BaA'' (dried at 140°).—K_2A''.—Na_2A'' *x*aq.—PbA'' (dried at 130°).

Isomer.—Ammonia converts the acid into a brown amorphous base, isomeric with it (Limpricht, *B.* 18, 1472; Bauer, *A.* 229, 360).

***m*-Thio-sulpho-benzene-azo-benzene-*m*-thio-sulphonic acid**

[3:1] $HS.SO_2.C_6H_4.N_2.C_6H_4.SO_2.SH$ [1:3]. [91°-93°]. From its salts by adding *glacial* acetic acid. A voluminous yellow pp. insol. water or alcohol, and resinified when boiled with them (Limpricht, *B.* 18, 1471; Bauer, *A.* 229, 358).

Barium salt.—BaA''5aq. One of the products of the action of baric sulphydrate upon the chloride of sulpho-benzene-azo-benzene-sulphonic acid (*q. v.*). V. sol. hot water, sl. sol. cold water, nearly insoluble in alcohol. Yellow ammonic sulphide slowly converts it into the corresponding hydrazo- compound.

Na_2A''*x*aq. Its solutions give amorphous pps. with salts of Cu, Pb, Ag and Fe'''.

***p*-Thio-sulpho-benzene-azo-benzene-thiosulphonic acid**

[4:1] $C_6H_4(SO_2SH)—N_2—C_6H_4(SO_2SH)$ [1:4]. Yellow amorphous solid. Sl. sol. water and alcohol. Formed by the action of a saturated aqueous solution of $Ba(SH)_2$ upon the chloride of sulpho-benzene-azo-benzene-sulphonic acid. Na_2A''*x*aq: very soluble yellow warty crystals.—BaA'': yellow warty crystals, sol. hot water (Limpricht, *B.* 18, 1474; Bauer, *A.* 229, 368).

***p*-Toluene-azo-aceto-acetic acid**

[4:1] $C_6H_4(CH_3)—N_2—CH(CO.CH_3).CO_2H$. [188°].

Ethyl ether A'Et: [70°]; yellow needles. Formed by the action of *p*-diazo-toluene chloride on an alcoholic solution of sodio-acetacetic ether (Züblin, *B.* 11, 1419; Richter a. Münzer, *B.* 17, 1929).

***p*-Toluene-azo-acetone**

[4:1] $C_6H_4(CH_3)—N_2—CH_2.CO.CH_3$. [115°].

Formation.—1. By heating *p*-toluene-azo-aceto-acetic ether with a dilute alcoholic solution of NaOH.—2. By heating *p*-toluene-azo-aceto-acetic acid above its melting-point, CO_2 being evolved (Richter a. Münzer, *B.* 17, 1929). Yellow needles. Sl. sol. water.

Toluene-azo-bromo-toluene

$C_6H_4Me—N_2—C_6H_3BrMe$. *Bromo-azo-toluene.* [136°] (P.); [138·5°] (J. a. E.). Formed by brominating *p*-toluene-*p*-azo-toluene (Petrieff, *B.* 6, 557; Janovsky a. Erb, *B.* 20, 363). Golden plates or needles. Reduces to a hydrazo- compound [119°].

Toluene-azo-chloro-toluene

[4:1] $C_6H_4Me.N_2.C_6H_3MeCl$ [1:5:2]. [97°]. Formed by the action of cuprous chloride upon diazotised *p*-toluene-*p*-azo-toluidine (from *p*-toluidine); yield, 20 p.c. of theoretical. Brown plates. V. sol. alcohol, ether, and benzene (Mentha, *B.*19, 3026).

***p*-Toluene-azo-*p*-cresol**

[4:1] $C_6H_4(CH_3)—N_2—C_6H_3(CH_3)(OH)$ [1:5:2] [113°]. Obtained by the action of *p*-diazo-toluene chloride on an alkaline solution of *p*-cresol. It is also formed by diazotising *p*-toluene-azo-*p*-toluidine $C_6H_4(CH_3)—N_2—C_6H_3(CH_3)(NH_2)$ and boiling the product with water (Nölting a. Kohn, *B.* 17, 354). Reddish needles or yellow tables. V. sol. ether, benzene, and hot alcohol.

Acetyl derivative [91°], yellow needles.

Benzoyl derivative [95°], small yellow needles.

***o*-Toluene-azo-ethyl-(β)-naphthyl-amine**

[2:1] $C_6H_4(CH_3)—N_2—C_{10}H_6(NHEt)$ [1:2]. [132°]. Formed by heating ethyl-(β)-naphthyl-nitrosamine with an acetic acid solution of *o*-toluidine (Henriques, *B.* 17, 2670).

***p*-Toluene-azo-ethyl-(β)-naphthyl-amine**

[4:1] $C_6H_4(CH_3).N_2.C_{10}H_6(NHEt)$ [1:2]. [113°]. Formed by heating ethyl-(β)-naphthyl-nitrosamine with an acetic acid solution of *p*-toluidine (Henriques, *B.* 17, 2670).

***o*-Toluene-*p*-azo-(α)-naphthol**

[2:1] $C_6H_4Me.N_2.C_{10}H_6(OH)$ [1:4]. *(α)-Naphthoquinone-o-tolyl-hydrazide.* [146°].

Formation.—1. From *o*-diazo-toluene and (α)-naphthol.—2. From (α)-naphthoquinone and *o*-tolyl-hydrazine.

Properties.—Red glistening needles. V. sol. alcohol, acetic acid, and benzene, less readily in benzoline. HNO_3 converts it into di-nitro-(α)-naphthol. With HCl and HBr it gives dark blue metallic-glistening salts. Dissolves in dilute NaOH.

Methyl ether $C_{17}H_{13}N_2(OMe)$ [93°]; reddish-brown glistening needles; easily soluble in ordinary solvents.

Ethyl ether $C_{17}H_{13}N_2(OEt)$ [94°]; red plates or dark thick needles (Zincke a. Rathgen, *B.* 19, 2488).

p-Toluene-p-azo-(α)-naphthol
[4:1] $C_6H_4Me.N_2.C_{10}H_6(OH)$ [1:4]. (α)-*Naphthoquinone-p-tolyl-hydrazide.* [208°].

Formation.—1. From *p*-diazo-toluene and (α)-naphthol.—2. From (α)-naphthoquinone and *p*-tolyl-hydrazine.

Properties.—Metallic-glistening dark-red spangles. V. sol. acetone, aniline, and hot nitrobenzene, sl. sol. alcohol, acetic acid, and benzene. Dissolves in dilute NaOH. HNO_3 converts it into di-nitro-(α)-naphthol. Not attacked by bromine in acetic acid solution. With mineral acids it forms salts which separate in bluish-green metallic-glistening plates. By heating with baryta-water it is rendered insoluble in alkalis.—B'HCl.—B'HBr.

Methyl ether $C_{17}H_{13}N_2(OMe)$ [104°].

Ethyl ether $C_{17}H_{13}N_2(OEt)$ [127°], large red crystals or red needles.

Acetyl derivative $C_{17}H_{13}N_2(OAc)$ [102°], fine yellowish needles (from benzoline) (Zincke a. Rathgen, *B.* 19, 2486).

o-Toluene-o-azo-(α)-naphthol
[2:1] $C_6H_4Me.N_2.C_{10}H_6(OH)$ [2:1] or

$C_6H_4Me.HN{<}\overset{O}{|}{>}C_{10}H_6$. (β)-*Naphtho-quinone-o-tolyl-hydrazide.* [156°]. Formed by the action of *o*-tolyl-hydrazine upon (β)-naphthoquinone. Glistening red plates. Easily soluble in ordinary solvents. HNO_3 converts it into di-nitro-(α)-naphthol. Bromine gives a di-bromo-derivative [254°] (Zincke a. Rathgen, *B.* 19, 2492).

p-Toluene-o-azo-(α)-naphthol
[4:1] $C_6H_4Me.N_2.C_{10}H_6(OH)$ [2:1] or

$C_6H_4Me.N_2H{<}\overset{O}{\frown}{>}C_{10}H_6$. (β)-*Naphtho-quinone-p-tolyl-hydrazide.* [145°]. Formed by the action of *p*-tolyl-hydrazine upon (β)-naphthoquinone. Red slender glistening needles. V. sol. alcohol, benzene, and acetic acid, sparingly in benzoline. By $SnCl_2$ it is reduced to (β)-amido-(α)-naphthol and *p*-toluidine. HNO_3 converts it into di-nitro-(α)-naphthol. Bromine gives a di-bromo-derivative [236°] (Zincke a. Rathgen, *B.* 19, 2491].

p-Toluene-o-azo-(β)-naphthol
[4:1] $C_6H_4Me.N_2.C_{10}H_6(OH)$ [1:2] or

$C_6H_4Me.N_2H{<}\overset{O}{\frown}{>}C_{10}H_6$. [135°]. Formed by combination of *p*-diazo-toluene with (β)-naphthol. Thick red needles or tables. V. sol. alcohol, benzene, acetic acid, and acetone. Insoluble in cold dilute NaOH. With acids it forms unstable salts. Bromine in acetic acid converts it into a di-bromo-derivative [190°]. HNO_3 gives di-nitro-(β)-naphthol (Zincke a. Rathgen, *B.* 19, 2490).

o-Toluene-o-azo-(β)-naphthol
[2:1] $C_6H_4Me.N_2.C_{10}H_6(OH)$ [1:2] or

$C_6H_4Me.N_2H{<}\overset{O}{\frown}{>}C_{10}H_6$. [131°]. Formed by combination of *o*-diazo-toluene with (β)-naphthol. Fine red needles or plates. Insol. cold dilute NaOH. With acids it forms unstable salts. HNO_3 converts it into di-nitro-(β)-naphthol. Bromine forms a mono-bromo-derivative [167°]. Zincke a. Rathgen, *B.* 19, 2491; Fischer, *B.* 20, 580).

p-Toluene-azo-(β)-naphthol disulphonic acid
$C_6H_4Me{-}N_2{-}C_{10}H_4(OH)(SO_3H)_2$. From sodium-(β)-naphthol disulphonate and *p*-diazo-toluene nitrate (Stebbins, *A. C. J.* 2, 236; *C. N.* 42, 44). Red leaflets, v. sol. water. Scarlet dye. The corresponding *o*- compound dyes yellower, the *m*- compound, redder.

p-Toluene-azo-(α)-naphthylamine
[4:1] $C_6H_4(CH_3){-}N_2{-}C_{10}H_6.NH_2$ [1:4]. [145°]. Prepared by the action of *p*-diazo-toluene sulphate on (α)-naphthylamine (Weselsky a. Benedikt, *B.* 12, 229). Red leaflets; insol. water.—$B'_2H_2SO_4$ 3aq: steel-blue needles.

o-Toluene-azo-nitro-ethane
[2:1] $C_6H_4Me{-}N_2{-}CH(NO_2).CH_3$. [88°]. From *o*-diazo-toluene nitrate and potassium nitro-ethane (Barbieri, *B.* 9, 387). Unstable orange needles.—NaA': golden spangles.

p-Toluene-azo-nitro-ethane. [133°]. Prepared like the preceding (B.). Orange prisms with steel-blue lustre. Its alkaline solutions are deep red.

Toluene-azo-nitro-toluene
$C_6H_4Me{-}N_2{-}C_6H_3(NO_2)Me$. *Nitro-azo-toluene* [114°]. Among the products of the nitration of toluene-azo-toluene dissolved in glacial acetic acid (Janowsky a. Erb, *B.* 20, 363). Orange monoclinic needles (from 90 p.c. alcohol).

Toluene-azo-nitro-toluene. [76°]. From toluene-azo-toluene and HNO_3 (S.G. 1·4) (Petrieff, *B.* 6, 557).

o-Toluene-azo-orcin
$C_6H_4Me{-}N_2{-}C_6H_2Me(OH)_2$ [203°–206°]. From *o*-diazo-toluene and orcin (Sciehilone, *G.* 12, 223). Red-brown crystals.

p-Toluene-azo-thymol sulphonic acid
$C_6H_4(CH_3){-}N_2{-}C_6H(CH_3)(C_3H_7)(HSO_3)OH$. Prepared by the action of *p*-diazo-toluene-chloride on sodium thymol-sulphonate.—A'Na: slender yellow needles; sol. alcohol and hot water, almost insoluble in cold water (Stebbins, *B.* 14, 2795).

o-Toluene-o-azo-toluene
[2:1] $Me.C_6H_4{-}N_2{-}C_6H_4.Me$ [1:2]. *o-Azo-toluene* [55°].

Preparation.—1. By distilling *o*-nitro-toluene with alcoholic potash; or by reducing it with zinc-dust and alcoholic NaOH (Schultz, *B.* 17, 497). Cannot be prepared by reducing *o*-nitro-toluene in alcoholic solution with sodium-amalgam (Perkin).—2. From *o*-toluidine and $KMnO_4$ (Hoogewerff a. van Dorp, *B.* 11, 1203).

Properties.—Dark red trimetric prisms; $a:b:c = 2·225:1:1·708$. Volatile with steam. Gives a mono-nitro- derivative [c. 67°], a di-nitro-derivative [142°], and a tri-nitro-derivative that decomposes before melting (Petrieff).

m-Toluene-m-azo-toluene
[3:1] $Me.C_6H_4{-}N_2{-}C_6H_4Me$ [1:3]. *m-Azo-toluene* [51°] (G.); [55°] (B.). From *m*-nitro-toluene by boiling with alcoholic KOH (Goldschmidt, *B.* 11, 1624), or by treatment with zinc-dust and alcoholic KOH (Barsilowsky, *B.* 10, 2097; *A.* 207, 114). Orange-red trimetric tables, $a:b:c = ·85:1:·54$. V. sol. alcohol.

p-Toluene-p-azo-toluene. *p-Azo-toluene*
[4:1] $Me.C_6H_4{-}N_2{-}C_6H_4Me$ [1:4]. [144°].

Formation.—From *p*-toluidine and CrO_3 in glacial acetic acid; or by treating a solution of *p*-toluidine in chloroform with bleaching-powder (R. Schmitt, *J. pr.* [2] 18, 198). Or by oxidising *p*-toluidine with H_2O_2 (Leeds, *B.* 14, 1382), or benzoyl peroxide. Cannot be prepared by distilling *p*-nitro-toluene with alcoholic potash

(Perkin), for by such treatment a red condensation product is obtained which on further reduction gives di-ami lo-di-phenyl-ethylene [227°]. (Bender a. Schultz, *B.* 19, 3237).

Preparation.—*p*-Nitro-toluene (20g.) in alcohol is treated with sodium-amalgam added gradually, the mixture being frequently cooled. The brown solid that separates is crystallised from glacial acetic acid (Perkin, *C. J.* 37, 554, *cf.* Jaworsky, *J. pr.* 94, 283; Werigo, *Z.* 1864, 640; Alexejeff, *Z.* 1866, 269; Melms, *B.* 3, 549; Schultz, *B.* 17, 472).

Properties. Red trimetric needles. V. sol. alcohol and ligroïn, sl. sol. alcohol. Slowly reduced to hydrazo-toluene by ammonium sulphide. In alcoholic solution it is reduced by $SnCl_2$ and HCl to tolidine [91°]. (S.). Nitric acid forms a mono-nitro- derivative, [76°], a dinitro- derivative [110°], and a tri-nitro- derivative [201°] (Petrieff).

***o*-Toluene-*m*-azo-toluene**
[2:1] $C_6H_4(CH_3)—N_2—C_6H_4(CH_3)$ [1:3]. Obtained by diazotising *o*-toluene-azo-*o*-toluidine (from *o*-toluidine) and treating the diazo- compound with alcohol (Schultz, *B.* 17, 470). Red oil. Volatile with steam. V. sol. alcohol and ether. By $SnCl_2$ and HCl in alcoholic solution it is converted into an unsymmetrical tolidine.

***m*-Toluene-*p*-azo-toluene**
[4:1] $C_6H_4(CH_3)—N_2—C_6H_4(CH_3)$ [1:3]. [58°].

Formation.—1. By the action of zinc-dust and alcohol upon *o*-diazo-toluene-azo-toluene.—2. By the action of Ag_2O and alcohol upon the compound $C_{14}H_{14}N_4$ the reduction-product of *o*-diazo-toluene-azo-toluene (Zincke a. Lawson, *B.* 19, 1458). Brownish-red plates. V. sol. alcohol, ether and benzene.

***o*-Toluene-azo-*o*-toluidine**
[2:1] $C_6H_4(CH_3)—N_2—C_6H_3(CH_3)(NH_2)$ [1:3:4] [100°]. Formed by passing nitrous acid gas into o-toluidine (Nietzki, *B.* 10, 662). Trimetric crystals, $a:b:c = 1·0116:1:1·3268$. Heated with aniline hydrochloride and alcohol at 160° it forms a red dye resembling saffranin.

Salts.—B'HCl: orange tables.—$B'_2H_2PtCl_6$.

Acetyl derivative
$C_7H_7—N_2—C_7H_6(NHAc)$. [185°]. Slender red needles, v. sol. alcohol (Schultz, *B.* 17, 469).

***m*-Toluene-azo-*m*-toluidine**
[3:1] $C_6H_4Me—N_2—C_6H_3Me(NH_2)$ [1:2:4]. [80°]. Formed by treating an alcoholic solution of *m*-toluidine with nitrous acid gas (Nietzki, *B.* 10, 1155). Golden needles. — B'HCl. — $B'_2H_2PtCl_6$. Gives *p*-tolylene diamine, [64°], on reduction.

***p*-Toluene-azo-*o*-toluidine**
[4:1] $C_6H_4Me—N_2—C_6H_3Me(NH_2)$ [1:3:4]. [128°]. From *p*-diazo-toluene toluide and *o*-toluidine hydrochloride (Nietzki, *B.* 10, 832). Gives *p*-tolylene-diamine, [64°], on reduction. Heated with aniline hydrochloride it forms a violet dye. Salts.—B'HCl.—$B'_2H_2PtCl_6$.

***p*-Toluene-azo-*m*-toluidine**
[4:1] $C_6H_4Me—N_2—C_6H_3Me(NH_2)$ [1:2:4]. [127°]. From *p*-diazo-toluene toluide and *m*-toluidine hydrochloride in alcoholic solution (Nietzki, *B.* 10, 1156). Large yellow plates. Gives *p*-tolylene-diamine [64°] on reduction.

Salts.—B'HCl.—$B'_2H_2PtCl_6$.

***p*-Toluene-azo-*p*-toluidine**
[4:1] $C_6H_4Me—N_2—C_6H_3Me(NH_2)$ [1:5:2] or $\left.\begin{array}{l} NH \\ | \\ C_6H_4Me.N_2H \end{array}\right\rangle C_6H_3Me$. [119°]. *o-Amido-azo-toluene.* Toluene-hydrazimido-toluene. Prepared by heating *p*-diazo-toluene-*p*-toluide (diazo-amido-toluene), dissolved in 5 or 6 times its weight of melted *p*-toluidine, with *p*-toluidine hydrochloride (1 mol.) at 65° for 12 hours. Orange-red glistening needles. V. sol. hot alcohol, acetic ether, and benzene. On reduction it gives *p*-toluidine and tolylene-*o*-diamine. CrO_3 oxidises it in acetic acid solution to toluene-azimido-toluene $C_7H_7—N_3—C_7H_6$ (Zincke, *B.* 18, 3142). Heated with *p*-toluidine hydrochloride and *p*-toluidine at 100° it gives a body $C_{28}H_{41}N_5$ analogous to azophenine which forms flat red needles. Heated to a higher temperature dyestuffs of the induline series are formed. It is converted into eurhodine $C_{17}H_{13}N_3$ by heating with (α)-naphthylamine hydrochloride (Witt, *C. J.* 49, 393). The salts of *o*-amido-azo-*p*-toluene are yellow in the solid state, but dissolve to green solutions.—B'HCl: slender light-yellow needles.

Acetyl derivative. [157°]; yellow felted needles.

Benzoyl derivative. [135°]; orange-yellow needles (Witt a. Nölting, *B.* 17, 77).

Disulphonic acid $C_{14}H_{13}N_3(SO_3H)_2$. Formed by sulphonating with fuming H_2SO_4 (N. a. W.). Greyish white needles. Is a yellow dyestuff of redder shade than 'acid yellow.'—$BaA''4aq$: brownish-red crystalline powder.

***p*-Toluene-azo-tolylene-diamine**
[4:1] $C_6H_4Me—N_2—C_6H_2Me(NH_2)_2$ [1:3:4:6]. [183°]. From *p*-diazo-toluene nitrate and tolylene-*m*-diamine (Hofmann, *B.* 10, 218). Orange needles, v. sol. alcohol, insol. water.—B''HCl.—$B''_2H_2PtCl_6$.

Xylene-azo-(β)-naphthol-(β)-sulphonic acid. Diazo-xylene does not combine with Rumpf's 'α'-sulphonic acid of (β)-naphthol in *dilute* alkaline solution, although some other diazo- compounds (such as diazo-benzene) do combine with it under the same conditions. If, however, the solution is very concentrated, the combination with diazo-xylene takes place. The product forms red needles, dissolves in H_2SO_4 with a red colour, and dyes wool a somewhat yellower shade than the compound from Schäfer's 'β'-acid (Schultz, *B.* 17, 461).

Xylene-azo-thymol-sulphonic acid
$C_6H_3(CH_3)_2—N_2—C_6H(CH_3)(C_3H_7)(HSO_3)OH$. Slender yellow needles. Prepared by the action of diazo-xylene chloride on sodium thymol-sulphonate.—A'_2Ba: small yellow needles or plates (Stebbins, *B.* 14, 2795).

Xylene-azo-xylene
$C_6H_3(CH_3)_2—N_2—C_6H_3(CH_3)_2$. *Azo-xylene* [126° corr.] Formed by reduction of nitro-*m*-xylene with sodium-amalgam or with zinc-dust and alcoholic NaOH; very small yield. A better yield is obtained by oxidation of xylidine with alkaline potassium ferricyanide (Werigo, *Z.* 1864, 723; 1865, 312; Samonoff, *Bl.* [2] 39, 597; *J. R.* 1882, 327; Schultz, *B.* 17, 476). Red needles. Sol. hot alcohol. It does not appear to give a dixylyl base by treatment with $SnCl_2$ and HCl in alcoholic solution.

***m*-Xylene-*o*-azo-*m*-xylidine**
[2:4:1] $C_6H_3Me_2—N_2—C_6H_2Me_2(NH_2)$ [1:3:5:6]
or $\left.\begin{array}{l} NH \\ | \\ C_6H_3Me_2—N_2H \end{array}\right\rangle C_6H_2Me_2$. *o-Amido-azo-xylene.* [78°]

Preparation.—Diazo-*m*-xylene-*m*-xylide, prepared by adding a solution of 1 mol. of sodium nitrite to a mixture of 1 mol. of *m*-xylidine $C_6H_3Me_2.NH_2$[1:3:4] and 1 mol. of its hydrochloride, is dissolved in *m*-xylidine and gently warmed for a long time with about 5 p.c. of *m*-xylidine hydrochloride. The mixture is then acidified with dilute HCl, the precipitated hydrochloride is filtered off, washed with water, alcohol, and ether, basified, and crystallised from alcohol or benzene; the yield is 70 p.c. to 80 p.c. of theoretical. Orange plates. V. sol. benzene, and hot alcohol, v. sl. sol. water.

Reactions.—On reduction it yields *m*-xylidine and *m*-xylylene-*o*-diamine $C_6H_2Me_2(NH_2)_2$ [1:3:5:6].

Salts.—B'HCl: yellow crystalline powder, dissolves sparingly in alcohol with a green colour, soluble in phenol with a splendid green colour (Nölting a. Forel, *B.* 18, 2682).

***m*-Xylene-*p*-azo-*m*-xylidine**
[2:6:1] $C_6H_3Me_2—N_2—C_6H_2Me_2(NH_2)$ [1:3:5:4] [78°]. Yellow plates. Easily soluble in alcohol and benzene. Prepared from *m*-xylidine $C_6H_3Me_2.NH_2$[1:3:2] by the same method as that described under *m*-xylene-*o*-azo-*m*-xylidine.

Salts.—$B'_2H_2Cl_2PtCl_4$: red crystalline powder. The hydrochloride dissolves in phenol or alcohol with a red colour (Nölting a. Forel, *B.* 18, 2684).

***m*-Xylene-*p*-azo-*m*-xylidine**
[3:5:1] $C_6H_3Me_2—N_2—C_6H_2Me_2(NH_2)$ [1:2:6:4]. [95°]. Prepared from *m*-xylidine $C_6H_3Me_2NH_2$ [1:3:5] by the same method as that described for *m*-xylene-*o*-azo-*m*-xylidine. Yellow plates. On reduction it gives symmetrical *m*-xylidine and *m*-xylylene-*p*-diamine $C_6H_2Me_2(NH_2)_2$ [1:3:2:5]. The hydrochloride dissolves in phenol with a violet-red colour (Nölting a. Forel, *B.* 18, 2684).

***o*-Xylene-*p*-azo-*o*-xylidine**
[2:3:1] $C_6H_3Me_2—N_2—C_6H_2Me_2(NH_2)$ [1:2:3:4]. [111°]. Prepared from *o*-xylidine $C_6H_3Me_2.NH_2$ [1:2:3] by the same method as that described under *m*-xylene-*o*-azo-*m*-xylidene (Nölting a. Forel, *B.* 18, 2684). Glistening yellow plates (from alcohol or benzene). On reduction it yields *o*-xylidine and *o*-xylylene-*p*-diamine $C_6H_2Me_2(NH_2)_2$[1:2:3:6]. The hydrochloride dissolves in phenol with a red colour.

***m*-Xylene-*p*-azo-*p*-xylidine**
[2:4:1] $C_6H_3Me_2—N_2—C_6H_2Me_2(NH_2)$ [1:2:5:4]. [111°]. Red plates.

Preparation: 50 c.c. of a solution of sodium nitrite containing 227 grms. $NaNO_2$ per litre are added to a mixture of 20 grms. of *p*-xylidine and 26 grms. of hydrochloride of *m*-xylidine $C_6H_3Me_2(NH_2)$ [1:3:4]; the diazoamide so formed is dissolved in 20 grms. of *p*-xylidine and gently warmed with 4 grms. of *p*-xylidene hydrochloride.

Reactions.—On reduction it yields *m*-xylidine and *p*-xylylene-*p*-diamine $C_6H_2Me_2(NH_2)_2$[1:4:2:5]. The hydrochloride dissolves in phenol with a red colour (Nietzki, *B.* 13, 470; Nölting a. Forel, *B.* 18, 2686).

***p*-Xylene-*p*-azo-*p*-xylidine**
[2:5:1] $C_6H_3Me_2—N_2—C_6H_2Me_2(NH_2)$ [1:2:5:4]. **[150°]. Red plates (from alcohol). Prepared from *p*-xylidine $C_6H_3Me_2(NH_2)$ [1:4:5] by the same method as that described under *m*-xylene-*o*-azo-*m*-xylidine. On reduction it yields *p*-xylidine and *p*-xylylene-*p*-diamine $C_6H_2Me_2(NH_2)_2$** [1:4:2:5]. The hydrochloride is red, and dissolves in phenol with a violet-red colour (Nölting a. Forel, *B.* 18, 2685).

***o*-Xylene-*o*-azo-*o*-xylidine**
[3:4:1] $C_6H_3Me_2—N_2—C_6H_2Me_2(NH_2)$ [1:3:4:6] or $\left.\begin{array}{l} NH \\ | \\ C_6H_3Me_2—N_2H \end{array}\right\rangle C_6H_2Me_2$. [179°]. Yellow plates. Sl. sol. alcohol. Prepared from *o*-xylidine $C_6H_3Me_2(NH_2)$ [1:2:4] by the same method as that described under *m*-xylene-*o*-azo-*m*-xylidine. On reduction it gives rise to *o*-xylidine and *o*-xylylene-*o*-diamine $C_6H_2Me_2(NH_2)_2$ [1:2:4:5]. Its hydrochloride dissolves in phenol with a green colour (Nölting a. Forel, *B.* 18, 2685).

DIAZO- COMPOUNDS. A class of bodies formed by the action of nitrous acid upon primary amido- compounds: $X.N\underline{H_2 + O}.N.OH = X.N_2.OH + H_2O$. They contain a pair of nitrogen atoms (Fr. *azote*) which are united to only one hydrocarbon radicle, whilst in the azo- compounds the N_2 group is united to two hydrocarbon radicles $X.N_2.Y$. The diazo-radicles $X.N'_2$ cannot of course exist in the free state, but they occur as hydrates $X.N_2.OH$, chlorides $X.N_2.Cl$, amides $X.N_2.NHR$, &c. For the sake of convenience reactions will usually be represented in this article as taking place with the hydrates.

The diazo- salts $X.N_2A$ may be regarded as derived from the salts of amines $X.NH_3A$ by the displacement of H_3 by N. This may take place in two ways. According to Kekulé's view, which is that most generally adopted, both nitrogen atoms are trivalent: X.N:N.A. On the other hand, Blomstrand (*Chemie der Jetztzeit*, p. 272, and *B.* 8, 51) assumes that the nitrogen attached to the carbon is pentavalent: $X.\underset{N}{\overset{}{N}}.A$; Strecker (*B.* 4, 786) and Erlenmeyer (*B.* 7, 1110) also concur in this view. The reduction of diazo- compounds to hydrazines, which have the undoubted constitution $X.NH.NH_2$, E. Fischer (*A.* 190, 67) regards as a proof of the correctness of Kekulé's formula, since a body of the constitution $X.\underset{N}{N}.A$ would, he considers, give on reduction $X.\underset{NH}{N}H_2$. Crum Brown, however, has pointed out in a private communication that this argument is fallacious, since the product of the reduction is not a hydrazine itself but a hydrazine-salt, and $X.\underset{N}{N}.A$, by adding H_2 to each N, would give the hydrazine salt $X.\underset{NH_2}{N}H_2A$. He considers the pentad N in the salts of hydrazines is most probably that connected to the hydrocarbon nucleus, in which case to explain their formation by adoption of Kekulé's formula would necessitate a shifting of the acid from one N to the other. The strongest argument against Kekulé's formula is that it represents diazo- salts, by not containing pentad nitrogen, as differently constituted to the salts of all other nitrogen bases. On the other hand, the

formula $X.\underset{N}{N}.A$ would necessitate a rearrangement of the molecule in the formation of azo-compounds which undoubtedly have the constitution X.N:N.Y.

The simplest member of the series $H.N_2.OH$ should be formed by the action of nitrous acid upon NH_3; but it has not yet been obtained, probably by reason of its extreme instability. The best-known diazo-compounds are those derived from aromatic amines and amido-compounds, some of which are tolerably stable bodies. No diazo-compounds have at present been obtained from fatty amines, for, like the first member of the series, $H.N_2.OH$, they are so unstable that they are probably scarcely capable of existence, and at once break up into the alcohol and N_2. The only known fatty diazo-compounds are a few which have lately been prepared from fatty amido-ethers (*e.g.* glycocoll). In their constitution they differ from the aromatic diazo-hydrates by containing a molecule of water less: $(EtO_2C)CH_2.N_2.OH - H_2O = (EtO_2C)CH{:}N_2$.

A. Aromatic diazo-compounds. The discovery of these bodies, and a large portion of our knowledge concerning them, are due to P. Griess (*A.* 106, 123; 113, 201; 117, 1; 120, 125; 121, 257; 137, 39; &c.), who, in a series of classical researches, opened up a field of investigation which in a few years has produced more discoveries of scientific interest and practical utility than almost any other branch of organic chemistry.

Formation.—1. By the action of nitrous acid, or any compound readily forming nitrous acid (*e.g.* NOCl, NOBr, $SO_2(OH)(NO_2)$, zinc-dust and HNO_3, &c.) upon salts of primary amines.—2. By oxidation of primary hydrazines (E. Fischer, *A.* 190, 97).

Preparation.—The details vary very much with individual cases and the purposes for which the diazo-compounds are required. The amine can be dissolved in water, alcohol, acetic acid, HCl, H_2SO_4, &c., and can then be treated with nitrous acid gas, sodium nitrite, or a nitrous ether. When required in the solid form, a common method is to mix the nitrate of the amine with a little water, cool in a freezing-mixture, and saturate with N_2O_3 gas; the diazo-nitrate is then ppd. by addition of alcohol and ether. Diazo-compounds can also be isolated from their aqueous solutions by ppn. as platino-chlorides, perbromides, picrates, sulphites, &c. When the diazo-compound is required for a subsequent reaction it is seldom necessary to isolate it, but the compound can be prepared under the conditions suitable to the second reaction. For instance, when the diazo-compound is to be conjugated with an amine or phenol to form an azo-compound, the amine is usually dissolved in water containing 2 mol. of HCl for each NH_2 group, cooled by addition of ice, and mixed with an aqueous solution of sodium nitrite (1 mol. to each NH_2). The solution of the diazo-chloride thus prepared can be at once treated with a solution of the phenol or amine.

The diazotisation of simple amines, in not too dilute solutions, usually takes place quantitatively, and the reaction is tolerably rapid. For instance, the diazotisation of aniline in a 10 p.c. solution is so complete within an hour that it forms the most accurate method of estimating nitrous acid or aniline (Green a. Rideal, *C. N.* 49, 173; Green a. Evershed, *S. C. I.* 1886, 633). The greater the molecular weight of the amine the slower and less complete is the diazotisation. The diazotisation of heavy amido-bodies is facilitated by the presence of a very large excess of mineral acid, using as little water as possible. Alcohol in many cases appears to have a contrary effect. Amido-groups cannot be diazotised unless combined with an acid: thus if the ordinary hydrochloride of *p*-phenylene diamine $C_6H_4(NH_2)(NH_3Cl)$ is treated with HNO_2 only one NH_2 group is diazotised; but if a large excess of HCl is employed so that $C_6H_4(NH_3Cl)_2$ is present, both NH_2 groups are diazotised. The final products of the action of nitrous acid upon the mono-acid salts of di-amines vary with the constitution of the latter. Thus *o*-phenylene diamine gives azimido-benzene:

$$C_6H_4(NH_2).N_2.OH - H_2O = C_6H_4\left\langle\begin{matrix} N \\ | \\ N \end{matrix}\right\rangle NH.$$

m-Phenylene diamine gives tri-amido-azo-benzene, thus: $C_6H_4(NH_2).N_2.OH + C_6H_4(NH_2)_2 = C_6H_4(NH_2).N_2.C_6H_3(NH_2)_2 + H_2O$. Whilst the diazo-compound $C_6H_4(NH_2).N_2.OH$ [1:4], from *p*-phenylene diamine, does not undergo any further transformation. The di-amido-benzoic acids react with nitrous acid in an exactly similar manner according as the NH_2 groups are *o*, *m*, or *p* to each other (Griess, *B.* 17, 607).

Properties.—The diazo-salts are in general very unstable crystalline solids. When dry they often decompose with detonation, by heat or percussion. Their solutions slowly decompose at the ordinary temperature, more quickly on heating, with evolution of nitrogen. The hydrates are even more unstable than the salts, and have scarcely ever been isolated. The stability is increased by substitution in the nucleus; thus diazo-benzene-sulphonic acid is more stable than diazo-benzene. The diazo-derivatives of substituted phenols and of *o*- and *p*- sulphonic acids usually occur in the form of anhydro-compounds, *e.g.*

$$C_6H_2Br_2\left\langle\begin{matrix} N_2.OH \\ OH \end{matrix}\right. - H_2O = C_6H_2Br_2\left\langle\begin{matrix} N_2 \\ | \\ O \end{matrix}\right., \text{ and}$$

$$C_6H_4\left\langle\begin{matrix} N_2.OH \\ SO_3H \end{matrix}\right. - H_2O = C_6H_4\left\langle\begin{matrix} N_2 \\ | \\ SO_3 \end{matrix}\right..$$

In a similar manner *o*-amido-diazo-compounds form inner amides (*e.g.* azimido-benzene, *v. supra*).

Reactions.—The diazo-compounds are extremely prone to undergo reactions; they play a most important part in organic syntheses and the determination of the constitution of isomeric aromatic compounds, by serving as an intermediate stage by means of which NH_2 groups can be replaced by H, OH, Cl, Br, I, F, CN, SH, NO_2, &c. Their power of combining with amines and phenols to form azo-compounds renders them of great technical importance for the production of colouring-matters, for which purpose they are prepared in large quantities. The majority of their reactions consist in the evolution of N_2, and its replacement by the atom or group (Cl, OH, &c.) previously united to it.

1. By *heating the aqueous solution* nitrogen is evolved, with formation of the corresponding phenol: $X.N_2.OH = X.OH + N_2$. The best method is to dissolve the amine in a considerable excess of dilute H_2SO_4, diazotise by adding $NaNO_2$ to the iced solution, and finally heat to boiling.

2. When heated with *strong alcohol* the normal reaction appears to be the replacement of the N_2 group by OEt, with formation of ethoxy-compounds (Wroblewski, *Z.* 6, 164; *B.* 17, 2703; Haller, *B.* 17, 1887; Hofmann, *B.* 17, 1917; Remsen, *Am.* 8, 243; *B.* 18, 65; Hayduck, *A.* 172, 212; Zander, *A.* 198, 25; Heffter, *A.* 221, 352; Paysan, *A.* 221, 212, 363; Mohr, *A.* 221, 222; Hesse, *A.* 230, 293).

3. Under certain circumstances, at present undetermined, the reaction with *alcohol* takes a different course, resulting in the substitution of H for the N_2 group, with production of the corresponding hydrocarbon together with aldehyde: $X.N_2.OH + C_2H_6O = X.H + C_2H_4O + N_2 + H_2O$ (Griess). (*a*) The amido-compound is treated with a solution of nitrous acid in absolute alcohol, warmed till nitrogen comes off freely, allowed to cool, resaturated with N_2O_3, and the operation repeated until but little gas is evolved on heating (Neville a. Winther, *C. J.* 37, 452). (*b*) The amido-compound is dissolved in a considerable excess of conc. H_2SO_4, the solution diluted with a small quantity of water is cooled in a freezing-mixture, and the necessary quantity of solid sodium nitrite added. When diazotised the solution is poured in a thin stream into two or three times its bulk of alcohol; the mixture becomes warm enough to complete the reaction without further heating (Meldola, *C. J.* 1885, 507).

4. *Mercaptan*, when heated with diazo-compounds at 170°, behaves similarly to alcohol in reaction 3, causing the displacement of N_2 by hydrogen with simultaneous formation of di-ethyl-di-sulphide (Schmitt a. Mittenzwey, *J. pr.* 126, 192).

5. The displacement of the N_2 group by H is also effected by reduction to the corresponding hydrazine (*q. v.*), and treatment of this with $CuSO_4$ or Fe_2Cl_6 (*B.* 18, 90).

6. Reduction of a diazo-chloride with excess of $SnCl_2$ also effects the displacement of N_2 by H: $X.N_2Cl + SnCl_2 + H_2O = X.H + SnOCl_2 + HCl + N_2$. A dilute aqueous solution of the diazo-chloride is treated with an excess of $SnCl_2$ at 0°, and finally heated for two hours with an inverted condenser; the yield is good (Effront, *B.* 17, 2329; Gasiorowski a. Wayss, *B.* 18, 337).

7. By treatment of a cold solution of a diazo-compound in conc. HCl with (2 mols. of) $SnCl_2$, the corresponding hydrazine (*q. v.*) is produced: $X.N_2.Cl + 2SnCl_2 + 3HCl = X.NH.NH_2 + 2SnCl_4$.

8. The reduction of the sulphites of diazo-compounds with SO_2, or with zinc-dust and acetic acid, also gives rise to hydrazines.

9. By heating with dilute HNO_3 nitrated phenols are obtained (Nölting a. Wild, *B.* 18, 1338).

10. The platino-chlorides on distillation with dry Na_2CO_3 yield the corresponding chloro-derivatives: $(X.N_2.Cl)_2PtCl_4 = 2X.Cl + 2N_2 + PtCl_4$.

11. The replacement of N_2 by Cl is also effected by boiling the diazo-compound with fuming HCl in large excess: $X.N_2.Cl = X.Cl + N_2$ (Griess, *B.* 18, 960; Gasiorowski a. Wayss, *B.* 18, 1936).

12. The same replacement is most readily effected by treating the aqueous solution of the diazo-chloride with *cuprous chloride*, which appears to act by intermediate formation of an addition product $R.N_2.Cl, Cu_2Cl_2$. (*a*) A 10 p.c. solution of Cu_2Cl_2 is prepared by adding 100 pts. of conc. HCl and 13 pts. of copper turnings to a hot solution of 25 pts. of crystallised $CuSO_4$ and 12 pts. of NaCl, boiling till decolourised, and making up the weight to 203 pts. with conc. HCl. A dilute HCl solution of the diazo-compound is allowed to run slowly into the above solution (about 5 times the weight of the amine used) heated nearly to boiling; the product, if volatile, is distilled with steam, or it is separated and purified by crystallisation. (*b*) In most cases instead of separately diazotising the amine, its solution in dilute HCl can be mixed with about 5 pts. of the 10 p.c. Cu_2Cl_2 solution, and a solution of the calculated quantity of $NaNO_2$ run into the nearly boiling mixture (Sandmeyer, *B.* 17, 1633, 2650; Lellmann, *B.* 19, 810).

13. The *perbromides* (*q. v.*) of diazo-compounds, on heating by themselves, or with dry Na_2CO_3, or best by boiling with *glacial acetic acid*, yield bromo-derivatives: $X.N_2.Br_3 = X.Br + Br_2 + N_2$ (Neville a. Winther, *C. J.* 37, 452).

14. The replacement of N_2 by Br is also effected by boiling the diazo-compound with fuming HBr in large excess: $X.N_2.Br = X.Br + N_2$ (Griess, *B.* 18, 960; Gasiorowski a. Wayss, *B.* 18, 1936).

15. The same replacement is most conveniently effected by means of *cuprous bromide* (*cf.* reaction 12). A solution of 125 pts. of crystallised $CuSO_4$ ($\frac{1}{2}$ mol.), 360 pts. of KBr (3 mols.), 800 pts. of water, and 110 pts. of conc. H_2SO_4 (1 mol.), is boiled with 200 pts. of copper-turnings till decolourised. The amine (1 mol.) is then added, and into the mixture, heated nearly to boiling, is slowly run a solution of 70 pts. $NaNO_2$ (1 mol.) in 400 pts. of water (Sandmeyer, *B.* 17, 2650; 18, 1492).

16. By boiling diazo-compounds with aqueous HI the N_2 group is replaced by I forming iodo-compounds: $X.N_2I = XI + N_2$ (Griess, *B.* 18, 960).

17. By boiling with HF the N_2 group is replaced by F giving fluoro-compounds: $X.N_2.F = XF + N_2$ (Griess, *B.* 18, 960; Paterno a. Oliveri, *G.* 12, 85; 13, 533; Wallach. *A.* 235, 255).

18. By heating diazo-salts with $Cu_2(CN)_2$ the N_2 group is replaced by CN (*cf.* reactions 12 and 15). The nitriles so formed can be converted into carboxylic acids by saponification, so that by means of this reaction an NH_2 group can be replaced by CO_2H. 28 pts. of KCN (96 p.c.) are added to a hot solution of 25 pts. of crystallised $CuSO_4$ in 150 pts. of water; into this solution, heated to about 90°, is slowly run an aqueous solution of the diazo-chloride. If the nitrile is required for conversion into the acid, it is not always necessary to isolate it, but the crude product of the reaction can be at once saponified (Sandmeyer, *B.* 17, 2650; 18, 1492, 1496).

19. By the action of a warm alcoholic solution of K_2S the N_2 group is replaced by SH, thus: $X.N_2.SH = X.SH + N_2$. The mercaptans so formed can be converted into sulphonic acids by oxida-

tion with cold $KMnO_4$; so that by means of this reaction an NH_2 group can be replaced by SO_3H (Klason, *B.* 20, 349).

20. *Hydric sulphide* converts diazo-benzene into phenyl sulphide $(C_6H_5)_2S$ (Graebe a. Mann, *B.* 15, 1683).

21. Diazo- compounds combine with *ethyl mercaptan* to form unstable bodies $X.N_2.SEt$, which when boiled with alcohol yield sulphides: $X.N_2.SEt = X.SEt + N_2$ (Stadler, *B.* 17, 2075).

22. By heating with *acetic anhydride*, acetylated phenols are formed: $X.N_2.OH + Ac_2O = X.OAc + N_2 + AcOH$ (Wallach, *A.* 235, 234).

23. SO_2 in presence of boiling alcohol converts some diazo- compounds into the corresponding sulphonic acids: $X.N_2.OH + SO_2 = X.SO_2.OH + N_2$ (Hubner, *B.* 10, 1715).

24. *Alkalis* give insoluble pps. of complex constitution (Frankland, *C. J.* 37, 750).

25. Action of *cyanogen compounds* (*v.* Griess, *B.* 9, 132; 12, 2119; Gabriel, *B.* 12, 1637).

26. *Cuprous nitrite* replaces the diazo- group by NO_2. The amine (1 mol.) is dissolved in exactly 2 mols. of dilute HNO_3 (or 1 mol. of dilute H_2SO_4) and the iced solution treated with one half of a solution of 2 mols. of $NaNO_2$, the other half being added when the diazotisation is complete. The solution of the diazo-nitrite is added to a paste of 1 mol. of Cu_2O (obtained by reducing $CuSO_4$ with glucose and NaOH) and the decomposition allowed to proceed in the cold. The yield of nitrobenzene from aniline is 42 p.c. of the theoretical, but with other bases it is smaller (Sandmeyer, *B.* 20, 1494).

27. *Primary and secondary amines*, react *at once* with diazo-compounds forming diazo-amides (*q.v.*): $X.N_2.OH + H_2N.Y = X.N_2.NHY + H_2O$. In these bodies the diazo- radicle replaces H united to N, and on treatment with excess of acid they readily regenerate the diazo- compound and amine. When diazo- compounds act upon *salts of aromatic amines*, the diazo- residue may replace H in the carbon-nucleus, with formation of amido-azo- compounds: $X.N_2.OH + HY''.NH_2 = X.N_2.Y''.NH_2 + H_2O$. In the case of tertiary aromatic amines the latter reaction is the only one possible, but with primary and secondary aromatic amines the replacement in the nucleus may be preceded by the formation of a diazo-amide, when there is no large excess of mineral acid present. The readiness with which amido-azo- compounds are formed varies greatly with the amine: in some cases (*e.g.* (α)- and (β)-naphthylamine, phenylene diamine, &c.) the replacement in the nucleus appears to take place almost instantly; in others (*e.g.* aniline) the reaction, at the ordinary temperature, takes several hours for its completion, allowing the intermediate formation of the diazo-amide (Friswell a. Green, *C. J.* 1885, 917; *Proceedings* 1887, 26). In many cases the formation of an amido-azo-compound will take place in presence of a large excess of acid, under which conditions the formation of a diazo-amide is precluded. In the formation of amido-azo- compounds of the benzene series the diazo-residue enters in the para- position to the NH_2 group; but when this place is already occupied it takes the ortho- position. The ortho-amido-azo- compounds appear to be differently constituted to the para-amido-azo-compounds (*v.* AZO- COMPOUNDS). If the amine does not contain any free para- or ortho- position the formation from it of an amido-azo- compound does not appear to be possible. When a diamine contains displaceable H atoms para to each NH_2 group, it is capable of reacting with 2 mols. of a diazo- compound to form a disazo- compound:

$$2X.N_2.OH + H_2.Y^{iv}(NH_2)_2 = (X.N_2)_2Y^{iv}(NH_2)_2 + 2H_2O.$$

28. Diazo - compounds readily react upon *phenols* and their sulphonic and carboxylic acids in alkaline solution, forming oxy-azo-compounds $X.N_2.OH + H.Y''.OH = X.N_2.Y''.OH + H_2O$. Compounds of the form $X.N_2.OY'$ analogous to the diazo-amides have never been obtained. The above remarks (*reaction* 24) with regard to the position taken by the diazo- group in the benzene-nucleus apply equally to oxy- and to amido-azo compounds. Also, the di-oxy- compounds, similarly to diamines, can give rise to disazo-compounds $(X.N_2)_2Y^{iv}(OH)_2$ when they contain displaceable H atoms para to each OH group.

29. Diazo- compounds readily react with *pyrrol*, with formation of azo- and disazo-bodies $X.N_2.C_4H_3NH$ and $(X.N_2)_2C_4H_2NH$, but no compounds analogous to diazo-amides (O. Fischer a Hepp, *B.* 19, 2251).

30. *Piperidine*, on the other hand, gives rise to piperidides $X.N_2.NC_5H_{10}$ (O. Wallach, *A.* 235, 233).

31. *Amido-thiophene*, unlike aniline, does not appear to form diazo-amides when treated with diazo- compounds, but gives at once amido-azo compounds $X.N_2.C_4SH_2.NH_2$ (Stadler, *B.* 18 2318). This is no doubt due to the tendency to replacement of the hydrogen being greater in the thiophene ring than in the benzene ring.

32. Diazo- compounds react with those bodies of the fatty series which contain H united to C, replaceable by sodium, *e.g.* nitro-methane, nitro-ethane, malonic ether, aceto-acetic ether, other ketonic ethers, &c. The products are mixed azo- compounds: those from nitro-methane, for instance, have the constitution $X.N_2.CH_2(NO_2)$ (Meyer, *B.* 8, 751, 1073; 9, 381; Zublin, *B.* 11, 1417; Kappeler, *B.* 12, 2286; Richter a. Münzer, *B.* 17, 1926; Griess, *B.* 18, 961; Bamberger, *B.* 17, 2415; 18, 2563).

Salts.—The diazo- salts have the general formula $X.N_2.A$. They are mostly white crystalline solids, very easily soluble in water, but sparingly in alcohol and ether. They are usually very unstable, and in the dry state are often very explosive, especially the nitrates and picrates. By the action of K_2SO_3 upon diazo- chlorides, sulphites are formed of the constitution $X.N_2.SO_3K$. Stannic and cuprous salts give double compounds of the formula $(X.N_2.Cl)_2SnCl_4$, $(X.N_2.Cl)Cu_2Cl_2$, $(X.N_2.Br)Cu_2Br_2$, &c. (Griess, *B.* 18, 965; Lellmann, *B.* 19, 810). The platino-chlorides $(X.N_2.Cl)_2PtCl_4$ are sparingly soluble pps. An excess of bromine produces yellow or red pps. of the per-bromides $X.N_2Br_3$. The diazo-sulphonic and carboxylic acids form salts $X''(SO_3M).N_2.OH$ with bases, as well as $X''(SO_3H).N_2.A$ with acids.

Amides. As already mentioned (*reaction* 27), the action of primary and secondary amines upon diazo- compounds gives rise to diazo-amides of the general formula $X.N_2.NHY$, or $X.N_2.NY_1Y_2$. Thus diazo-benzene and aniline

diazo-benzene-anilide(diazoamidobenzene): $H_5.N_2.OH + C_6H_5.NH_2 = C_6H_5.N_2.NH.C_6H_5$.

...e bodies are in general yellow crystalline ...s, stable below 100° when free from acid. ...reatment with an excess of mineral acid ... are resolved, even in the cold, into the ...o- salt and amine. When the amine is ...atic the resolution products again slowly ...bine, if the conditions are favourable, to ...ce an amido-azo- compound $X.N_2.Y''.NH_2$ ...ric with the original diazo- amide. The ...tion and recombination take place con...tly when the diazo-amide is treated with ...mol. of cold dilute HCl, or with unstable ...ts, such as $ZnCl_2$, $CaCl_2$, aniline chloride, &c., ...alcoholic or aniline solution (Friswell a. ...reen, *C. J.* 1885, 917; Wallach, *A.* 235, 233). When a diazo-amide is treated with a salt of a base different from that of which it is a compound, the diazo- salt generated will react upon that base of the two whose nucleal hydrogen is most readily replaced. Thus diazo-benzene-dimethyl-amide $C_6H_5.N_2.NMe_2$ treated with aniline chloride gives amido-azo-benzene and dimethyl-amine; similarly, diazobenzene-anilide $C_6H_5.N_2.NHC_6H_5$ treated with *m*-phenylene-diamine hydrochloride yields di-amido-azo-benzene $C_6H_5.N_2.C_6H_3(NH_2)_2$, whilst aniline is set free; but diazo-benzene-anilide treated with *p*-toluidine hydrochloride gives amido-azo-benzene and *p*-toluidine, because the para H of the aniline is more readily replaced than the ortho H of the *p*-toluidine. Even very weak acids, such as acetic acid and phenols, are capable of resolving most diazo-amides. In the latter case the diazo- compounds produced immediately combine with the phenol to form oxy-azo- compounds, for diazo- residues replace the hydrogen of the nucleus more readily in phenols than in amines (Heumann a. Oeconomides, *B.* 20, ...01).

In general it may be said that the reactions of the diazo-amides towards reagents in presence of acids, are simply the reactions of the free diazo- salts; thus $SnCl_2$ and HCl reduce them to hydrazines (*cf. reaction* 7); heating with strong halogen acids gives haloid derivatives of the hydrocarbons (*cf. reactions* 11, 14, 16, and 17); &c.

It appears to be proved (Griess, *B.* 7, 1619; Nölting a. Binder, *Bl.* 42, 336; Meldola a. Streatfeild, *C. J.* 1887, 102, 434) that the diazo-amides of the types $X.N_2.NHY$ and $Y.N_2.NHX$ are identical—that is, the same body is obtained whichever of the two amines is diazotised and combined with the other. The resolution of these unsymmetrical diazo-amides quite corresponds to their formation, for they yield a mixture of both diazo- compounds $X.N_2OH$ and $Y.N_2OH$, and both amines $X.NH_2$ and $Y.NH_2$. For instance, the compound $C_6H_5.N_3H.C_7H_7$ is obtained by combining either diazo-benzene with *p*-toluidine, or *p*-diazo-toluene with aniline; and on treatment with HCl it splits up equally into diazo-benzene, *p*-diazo-toluene, aniline, and *p*-toluidine. When only 1 mol. of HCl is present these resolution products will recombine to form one or more amido-azo- compounds according to circumstances.

Alkalis, even in boiling aqueous or alcoholic solution, usually have no action upon diazo-amides. The H of the NH group of the primary diazo-amides appears to have slightly acid properties, and by introduction of NO_2 groups into the nuclei the diazo-amide becomes sufficiently acid to dissolve in aqueous alkalis and form tolerably stable salts $X''(NO_2).N_2.NM'.Y(NO_2)$ (Meldola a. Streatfeild, *C. J.* 1886, 624; 1887, 102, 434).

By the action of alkyl haloids upon the primary diazo-amides dissolved in an alcoholic solution of (1 mol. of) sodium ethylate secondary diazo-amides are obtained (M. a. S.; Friswell a. Green, *B.* 19, 2034; *C. J.* 1886, 746). When the two aromatic nuclei are the same the secondary diazo-amides obtained by alkylation are identical with those got by direct combination of the diazo- compounds with secondary amines. But according to Meldola and Streatfeild (*C. J.* 1887, 434) the compound obtained by ethylating the unsymmetrical *m*-nitro-diazo-benzene-*p*-nitranilide [3:1] $C_6H_4(NO_2).N_3H.C_6H_4(NO_2)$ [1:4] (which is obtained either from *m*-nitro-diazo-benzene and *p*-nitraniline, or from *p*-nitro-diazo-benzene and *m*-nitraniline) is different from either of the two ethyl-derivatives [3:1] $C_6H_4(NO_2).N_2.NEt.C_6H_4(NO_2)$ [1:4] and [4:1] $C_6H_4(NO_2).N_2.NEt.C_6H_4(NO_2)$ [1:3], obtained by combining *m*- and *p*-nitro-diazo-benzene with ethyl-*p*- and *m*- nitranilines respectively. The two latter ethyl derivatives are split up by acids into *m*-nitro-diazo-benzene and ethyl-*p*-nitraniline, and *p*-nitro-diazo-benzene and ethyl-*m*-nitraniline respectively; but the former ethyl derivative (obtained by ethylation) yields both diazo-compounds and both ethyl-nitranilines in about equal amounts.

Constitution of diazo-amides.—Although a considerable amount of work has been done on this subject, the matter is still far from settled. The formula

$$X.N-N.Y \text{ with } \diagdown\diagup \text{ NH}$$

is disproved by the resolution of the alkyl derivatives into diazo- compound and alkylated amine, since the latter could not be obtained from a compound of that structure (Friswell a. Green, *C. J.* 1886, 746, and *B.* 19, 2034). The formula $X.\underset{N}{N}.NHY$ does not appear to have much probability, since one would expect a body of the constitution $C_6H_5.\underset{N}{N}.NHC_6H_5$ to give on reduction NH_3 and hydrazobenzene; these bodies, however, are not formed from diazo-benzene-anilide, even by adding sodium to its boiling alcoholic solution (F. a. G.). Neither the latter formula nor that usually assumed X.N:N.NHY is capable of explaining the existence of more than two isomeric alkyl derivatives.

For further references concerning the diazo-amides see Bayer a. Jäger, *B.* 8, 148, 893; Sarauw, *B.* 14, 2442; 15, 42; Nölting a. Baumann, *B.* 18, 1147; Staedel a. Bauer, *B.* 19, 1952; Wallach, *A.* 235, 233; Bernthsen a. Goske, *B.* 20, 926.

Imides.—Obtained by the action of NH_3 upon the per-bromides:

$$X.N_2Br_3 + NH_3 = X.N\begin{matrix}\diagup N\\ \| \\ \diagdown N\end{matrix} + 3HBr$$ (Griess, *A.* 137, 65; *B.* 18, 963). They are also formed by

the decomposition of nitroso-hydrazines: $\mathrm{X.N}{<}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{NO}\end{smallmatrix} = \mathrm{X.N}{<}\begin{smallmatrix}\mathrm{N}\\ \Vert\\ \mathrm{N}\end{smallmatrix} + \mathrm{H_2O}$ (Fischer, *A.* 190, 92, 96). They are usually yellowish oily liquids, insoluble in water, exploding when heated. When heated with conc. HCl they are converted into chloro-amido- compounds: $\mathrm{HX''.N_3 + HCl = X''Cl(NH_2) + N_2}$. Diazo-benzene-imide heated with H_2SO_4 diluted with an equal volume of water is converted into *p*-amido-phenol: $\mathrm{C_6H_5.N_3 + H_2O = C_6H_4(OH)NH_2 + N_2}$ (Griess, *B.* 19, 313; Fischer, *A.* 190, 67; 232, 236; Silberstein, *J. pr.* [2] 27, 116). Diazo-benzoic acid reacts with phenyl-hydrazine, forming the imides of diazo-benzoic acid and of diazo-benzene together with amido-benzoic acid and aniline, thus: $\mathrm{2C_6H_4}{<}\begin{smallmatrix}\mathrm{CO_2}\\ |\\ \mathrm{N_2}\end{smallmatrix} + \mathrm{2C_6H_5NH.NH_2} =$

$$\mathrm{C_6H_4(CO_2H).N}{<}\begin{smallmatrix}\mathrm{N}\\ \mathrm{N}\end{smallmatrix} + \mathrm{C_6H_5.N}{<}\begin{smallmatrix}\mathrm{N}\\ \mathrm{N}\end{smallmatrix} +$$

$\mathrm{C_6H_4(NH_2)CO_2H + C_6H_5.NH_2}$. This equation is general (Griess, *B.* 20, 1528).

Diazo- compounds derived from o-amido-azo- compounds.—Although the so-called *o*-amido-azo- compounds probably do not contain an NH_2 group, but are hydrazimido-bodies $\mathrm{X'{-}N}{<}\begin{smallmatrix}\mathrm{NH}\\ \mathrm{NH}\end{smallmatrix}{>}\mathrm{Y''}$ or $\begin{smallmatrix} & \mathrm{NH}\\ & |\\ \mathrm{X'{-}NH.N} & \end{smallmatrix}{>}\mathrm{Y''}$ they are, nevertheless, slowly attacked by nitrous acid, with production of diazo- compounds. The only member of this class of diazo- compounds at present examined is that obtained by diazotising *o*-amido-azo-toluene. In some of its reactions it behaves like an ordinary diazo-compound, in others quite differently. On heating with water or alcohol it is decomposed with evolution of nitrogen. By zinc-dust and alcohol it is converted into *m-p*-azotoluene and N_2. It is not reduced by $SnCl_2$ or SO_2 to a hydrazine, but gives a stable compound $C_{14}H_{14}N_4$ which probably has the constitution

$$\mathrm{C_6H_3(CH_3)}{<}\begin{smallmatrix}\mathrm{N{-}NH}\\ |\quad|\\ \mathrm{N{-}N.C_6H_4(CH_3)}\end{smallmatrix}.$$

This body is re-converted by bromine into the per-bromide of the original diazo-compound. The diazo-imide loses nitrogen on heating, and yields tolyl-azimido-toluene $\mathrm{C_6H_3(CH_3)}{<}\begin{smallmatrix}\mathrm{N}\\ |\\ \mathrm{N}\end{smallmatrix}{>}\mathrm{N.C_6H_4(CH_3)}$ identical with that obtained by oxidation of *o*-amido-azo-toluene (tolyl-hydrazimido-toluene). Hence the constitution of this peculiar diazo-compound is probably

$$\mathrm{C_6H_3(CH_3)}{<}\begin{smallmatrix}\mathrm{N{-}N.OH}\\ |\quad|\\ \mathrm{N{-}N.C_6H_4(CH_3)}\end{smallmatrix}$$

(Zincke a. Lawson, *B.* 19, 1452; 20, 1176).

B. Fatty diazo- compounds $\mathrm{X''}{<}\begin{smallmatrix}\mathrm{N}\\ \Vert\\ \mathrm{N}\end{smallmatrix}$. As already stated, the fatty diazo- compounds contain a molecule of water less than the aromatic diazo-hydrates. Their discovery is quite recent, and is due to Curtius. At present only a few members of the group are known; these are obtained by the action of $NaNO_2$ upon the hydrochlorides of amido-fatty-ethers $\mathrm{X'''H_2.CO_2R}$, and hence have the constitution $\mathrm{X'''(N_2)CO_2R}$. They are unstable oily bodies, which exhibit the following reactions:—1. By boiling with *water* or *dilute acids*, they are usually converted into oxy-ethers, *e.g.* $\mathrm{CH_2(OH)CO_2Et}$, with evolution of nitrogen; however, diazo-succinic ether $\begin{smallmatrix}\mathrm{C(N_2).CO_2Et}\\ |\\ \mathrm{CH_2.CO_2Et}\end{smallmatrix}$, by this treatment gives fumaric ether.—2. With *alcohols* they yield alkyl-oxy-ethers, *e.g.* $\mathrm{CH_2(OEt).CO_2Et}$.—3. With *organic acids* they yield alkoyl-oxy-ethers, *e.g.* $\mathrm{CH_2(OAc).CO_2Et}$.—4. With *aldehydes* they yield alkoyl-ethers, *e.g.* $\mathrm{CH_2Ac.CO_2Et}$.—5. With *zinc-dust* and *acetic acid*, they are reduced first to hydrazines, and then to the original amido-ethers.—6. *Iodine* in ethereal solution converts them into di-iodo-ethers, *e.g.* $\mathrm{CHI_2.CO_2Et}$; bromine and chlorine act similarly.—7. By long boiling with *aromatic hydrocarbons*, nitrogen is evolved, and condensation-products are formed.—8. By treatment with *conc. halogen acids* they yield haloid ethers, *e.g.* $\mathrm{CH_2Cl.CO_2Et}$.—9. By treatment of the diazo-ethers with NH_3 they are converted into the corresponding amides, *e.g.* $\mathrm{CH(N_2).CO.NH_2}$, whose reactions are similar to those of the ethers. The free diazo-acids, *e.g.* $\mathrm{CH(N_2).CO_2H}$, and their salts, have not yet been isolated, on account of their instability (Curtius, *B.* 17, 953; *B.* 18, 1283; Buchner a. Curtius, *B.* 18, 2371; 19, 850; Curtius a. Koch, *B.* 18, 1293; 19, 2460). A. G. G.

DESCRIPTION OF DIAZO- COMPOUNDS.

A large number of diazo- compounds are mentioned under the amido- compounds from which they are formed.

Pseudo-diazo-acetamide $C_6H_9N_9O_3$. Formed, together with diazoacetamide, by prolonged action of strong aqueous NH_3 in the cold upon the methyl ether of diazoacetic acid $\mathrm{CHN_2.CO_2Me}$ (Curtius, *B.* 18, 1287). Fine crystalline yellow powder, consisting of microscopic quadratic plates. Sl. sol. cold water, dilute HCl, and acetic acid. Insol. alcohol, ether, and benzene. Dibasic acid. On warming with water it evolves nitrogen. Aqueous alkalis evolve nitrogen and ammonia. It gives a green colouration with Fehling's solution; on boiling a black pp. is formed. Silver and mercury salts are reduced on boiling.

Salts.—$\mathrm{A''(NH_4)_2}$: small yellow tables; sl. sol. cold water [c. 155°].—$\mathrm{A''Ag_2}$ $1\frac{1}{2}$aq: yellow microcrystalline pp., v. sl. sol. water. Explodes on heating.—A'Hg: yellow pp.—$\mathrm{A''Cu''}$: sparingly soluble reddish-brown pp.—A''Pb: yellow pp.

Diazo-acetic acid $\mathrm{CHN_2.CO_2H}$. The free acid and its salts have not been isolated on account of their instability. The alkaline salts are obtained in solution by treating the methyl ether with cold aqueous alkalis.

Methyl ether MeA'. (129°) at 721 mm. S.G. ^{21} 1·139.

Ethyl ether EtA'. [−24°]. (144°) at 721 mm. S.G. ^{22} 1·073. Formed by the action of $NaNO_2$ on a concentrated solution of the hydrochloride of amido-acetic ether. Yellow oil. V. sl. sol. water; miscible with alcohol, ether, benzene, and light petroleum. Explodes when conc.

H_2SO_4 is poured upon it. *Reactions.*—1. Boiling *water* gives glycollic ether, nitrogen, and alcohol.—2. Boiling *alcohol* gives $CH_2(OEt).CO_2Et$ and nitrogen. — 3. *Benzoic acid* gives rise to $CH_2(OBz).CO_2Et$.—4. Reduces $AgNO_3$ in cold aqueous solution.—5. Reduces hot *Fehling's solution*.—6. *Zinc-dust* and acetic acid form an unstable hydrazo- derivative $NH_2.NHCH_2.CO_2Et$, which is further reduced to ammonia and $NH_2.CH_2.CO_2Et$. The hydrazo- derivative reduces cold Fehling's solution.—7. Combines with *aldehydes*, thus: $Ph.CHO + CHN_2.CO_2Et = Ph.CO.CH_2.CO_2Et + N_2$.—8. Changes on standing into 'azin-succinic' ether, $C_8H_{12}N_4O_4Et_4$ [245°]. 9. Boiling *aniline* produces $NPhH.CH_2.CO_2Et$.—10. Conc. HCl gives $CH_2Cl.CO_2Et$.—11. Hot conc. KOH forms a crystalline pseudo-diazo-salt whence boiling dilute H_2SO_4 liberates hydrazine, N_2H_4 (Curtius, *B.* 20, 1632).—12. Boiling aromatic hydrocarbons produce condensation products; thus benzene gives $C_7H_6CO_2Et$ (Buchner a. Curtius, *B.* 18, 2371).

Iso-amyl-ether $C_5H_{11}A'$. (160°) at 720 mm.

Amide $CHN_2.CONH_2$ [114°]; yellow tables or prisms; v. sol. cold water or alcohol. Formed by the action of strong aqueous NH_3 upon the methyl-ether. The aqueous solution decomposes on boiling with evolution of nitrogen and formation of glycollamide. By treatment in alcoholic solution with iodine it is converted into di-iodo-acetamide $CHI_2.CONH_2$ with evolution of nitrogen. It gives a blood-red colouration with $AgNO_3$, and in a few moments a reduction to metallic silver. It also reduces $Hg(NO_3)_2$ and $Cu(OAc)_2$. With Fehling's solution it produces a red colouration, which becomes green on boiling (Curtius, *B.* 17, 953; 18, 1283).

Diazo-amido-benzoic acid

$$\overset{(3)}{C_6H_3(NH_2)}\left\langle\begin{array}{l}CO.O\ (1)\\ \quad|\\ N{:}N\ (6)\end{array}\right.$$

Obtained by adding sodium nitrite to a solution of (6:3:1)-*p*-di-amido-benzoic acid containing barely sufficient HCl to dissolve it. Long slender needles, or four-sided plates. Yellow colour. Bitter taste. V. sol. hot water, sl. sol. hot alcohol, insol. ether. Has no acid properties, but is a weak base. When dry it explodes on heating. It is decomposed by long boiling with water. It combines with amines and phenols to form azo-compounds.

Salts.—B_2HCl: white six-sided plates.—$B_2H_2Cl_2PtCl_4$: sparingly soluble small yellow trimetric plates.—$B_2AuCl_3.HCl$: yellow insoluble needles (Griess, *B.* 17, 603).

***p*-Diazo-aniline salts** are formed by diazotising salts of *p*-phenylene-diamine (Griess, *B.* 17, 607).—$C_6H_4(NH_2)N_2ClHClAu_2Cl_6$ is an insoluble pp.

***m*-Diazo-aniline imide** $C_6H_4(NH_2).N\left\langle\begin{array}{l}N\\ \|\\ N\end{array}\right.$

m-Amido-diazo-benzene imide. Yellowish oil. Volatile with steam. Easily soluble in alcohol and ether.

Preparation.—*m*-Amido-phenyl-oxamic acid $C_6H_4(NH_2).NH.C_2O_2.OH$ is diazotised and converted into the tribromide $C_6H_4(N_2Br_3).NH.C_2O_2.OH$. By treatment with NH_3 this yields the imide $C_6H_4(N_3).NH.C_2O_2.OH$, which on boiling with aqueous KOH splits off the oxalyl group with production of *m*-diazo-aniline imide. On diazotisation it gives a diazo- compound which combines with phenols and amines to form azo-dyestuffs. Decomposes explosively on heating.

Salts.—B'HCl: white soluble trimetric plates.—$B'_2H_2Cl_2PtCl_4$: yellow needles (Griess, *B.* 18, 963).

***m*-Diazo-aniline piperidide.**

Acetyl derivative $C_6H_4(NHAc).N_2.NC_5H_{10}$. [101°]. From acetyl-*m*-tolylene-diamine hydrochloride by diazotisation and treatment with piperidine (Wallach, *A.* 235, 266).

(α)-Diazo-anthraquinone nitrate $C_{14}H_7O_2.N_2NO_3$. Formed by passing nitrous acid gas into a solution of (α)-amido-anthraquinone in dry ether (Böttger a. Petersen, *A.* 166, 150). Powder, m. sol. water, v. sol. alcohol, insol. ether. When heated with water it gives N_2 and *m*-oxy-anthraquinone.

Diazo-benzene. *References*: Griess, *Tr.* 1864, iii. 667; *A.* 113, 201; 137, 39.

Hydroxide $Ph.N_2.OH(?)$. On adding acetic acid to an aqueous solution of $Ph.N_2.OK$ a thick yellow oil is ppd.; this may be diazo-benzene hydroxide. It is very unstable.

Salts.—$Ph.N_2.OK$. A crystalline substance obtained by adding excess of conc. aqueous KOH to a saturated solution of diazo-benzene nitrate, and evaporating at 100°. Detonates feebly at 130°. V. sol. water and alcohol, insol. ether.—$Ph.N_2.OAg$: obtained as a greyish-white pp. on adding $AgNO_3$ to an aqueous solution of the preceding; explodes when heated.—$(Ph.N_2.O)_2Hg$: white pp. got by adding $HgCl_2$ to the potassium salt (Griess, *A.* 137, 57).

Nitrate. — $Ph.N_2.NO_3$. S.G. 1·37. H.F. −47,400 (Berthelot a. Vieille, *C. R.* 92, 1074). Prepared by passing nitrous fumes at 0° into an aqueous solution of aniline nitrate containing undissolved aniline nitrate in suspension; ppd. by adding alcohol and ether. Needles; v. e. sol. water, m. sol. alcohol, insol. ether and benzene. Stable in dry air in the dark, but decomposed in moist air. Explodes at 90° forming CO, CH_4, N, HCN, CH_4, and C. The decomposition may be roughly represented thus: $C_6H_5.N_2.NO_3 = 3CO + 3C + 5H + 3N$.

Reactions.—1. *Barium carbonate* added to its aqueous solution produces $Ph.N_2.C_6H_4.OH$ and $C_{18}H_{14}N_4O$ [131°]. This 'benzene-di-azo-phenol' is perhaps $C_6H_5.N_2.C_6H_3(OH).N_2.C_6H_5$ for it may be reduced by HI to di-amido-phenol (P. F. Frankland, *C. J.* 37, 751). It is soluble in NaOHAq.—2. Aqueous NaOH, added to neutralisation, gives the 'benzene-di-azo-phenol' and a brown substance, $C_{30}H_{23}N_5O$, insol. NaOHAq.—3. Aqueous *ammonia* produces diazo-benzene-anilide and two amorphous brown substances, $C_{18}H_{21}N_2O$ and $C_{12}H_{13}N_3O$. The latter is very explosive and is decomposed by boiling HCl into phenol, aniline, and N_2.—4. Boiling dilute HNO_3 (1 mol.) forms *o*- and *p*- nitro-phenol (Nölting a. Wild, *B.* 18, 1338).—5. Aqueous K_4FeCy_6 forms a compound $C_{18}H_{14}N_2$, [150°] (Griess, *B.* 9, 132). 6. *Potassic ferricyanide* gives $(C_6H_4N_2)_3(H_3FeCy_6)_2$. 7. *Sodium nitroprusside* gives the compound $C_6H_4N_2H_2FeCy_5(NO)aq$ (Griess, *B.* 12, 2120).—8. *Nitro-benzyl cyanide* and alcoholic KOH give a pp. of $C_{14}H_{10}N_4O_2$ [202°] (Perkin, *C. J.* 43, 111).

Chloride.—$Ph.N_2.Cl$. Formed in solution

by diazotising aniline hydrochloride. *Combinations.*—$(C_6H_5.N_2.Cl)_2SnCl_4$: white plates, sol. water, v. sl. sol. alcohol and ether (Griess, *B.* 18, 965).—$(PhN_2Cl)_2PtCl_4$: yellow prisms, v. sl. sol. water, insol. alcohol and ether.—$PhN_2ClAuCl_3$: golden plates, insol. water, m. sol. warm alcohol.

Bromide. $Ph.N_2.Br$. Formed by adding bromine to an ethereal solution of diazo-benzene amide, or by washing the perbromide for a long time with ether. Pearly plates, v. e. sol. water, insol. ether.

Perbromide.—$Ph.N_2.Br_3$. Formed by adding bromine dissolved in HClAq to an aqueous solution of a diazobenzene salt. Large yellow plates, insol. water and ether, m. sol. cold alcohol. Gives bromo-benzene when distilled with Na_2CO_3 or when heated with alcohol.

Sulphate. $Ph.N_2.SO_4H$. Ppd. by adding alcohol (3 vols.) and ether to a solution of diazobenzene nitrate mixed with an equivalent quantity of H_2SO_4. Prisms, v. e. sol. water, v. sl. sol. alcohol, insol. ether. Explodes at 100°.

Dicyanide. $C_8H_5N_4$ or $C_6H_5.N_2.CN,HCN$. [69°]. Formed by the action of a diazo-benzene salt on a solution of KCN. Readily decomposes (Gabriel, *B.* 12, 1637).

Picrate. $Ph.N_2.O.C_6H_2(NO_2)_3$. Yellow needles, obtained by mixing solutions of diazobenzene nitrate and sodium picrate. Very explosive (Baeyer a. Jäger, *B.* 8, 984).

Sulphite. The *potassium salt*, $C_6H_5.N_2.SO_3K$, called also *potassium diazobenzene sulphonate* is ppd. by adding KOH to a mixture of diazobenzene nitrate and K_2SO_3Aq (E. Fischer, *A.* 190, 73). It forms explosive yellow crystals. Bromine in conc. HBrAq pps. diazobenzene perbromide. Zinc-dust and acetic acid reduce it to the corresponding hydrazo- compound.

Nitrite. Converted by Cu_2O into nitro-benzene (Sandmeyer, *B.* 20, 1497).

Benzene-sulphinate $Ph.N_2.SO_2.C_6H_5$. [76°]. From sodium benzene sulphinate and diazobenzene nitrate (Königs, *B.* 10, 1532). Orange tables (from alcohol); insol. cold water, v. sol. alcohol and ether.

m-**Tetr-azo-benzene** $C_6H_4(N_2.OH)_2$ [1:3]. Formed by the action of a large excess of nitrous acid upon *m*-phenylene-diamine in presence of a large excess of HCl. It combines with 2 mols. of an amine or phenol.

Salts. $C_6H_4(N_2Cl)_2PtCl_4$: small yellow plates; nearly insoluble in cold water and alcohol; heated with dry Na_2CO_3 it yields di-chloro-benzene.—$C_6H_4(N_2Cl)_2Au_2Cl_6$: pp. of yellow microscopic needles, explosive (Griess, *B.* 19, 317).

p-**Tetr-azo-benzene** $C_6H_4(N_2.OH)_2$ [1:4]. Formed by the action of an excess of nitrous acid upon *p*-phenylene-diamine in presence of a large excess of acid. $C_6H_4(N_2Cl)_2PtCl_4$: yellow crystalline explosive pp.; by heating with dry Na_2CO_3 it yields *p*-di-chloro-benzene (Griess, *B.* 19, 319).

Diazo-benzene-*m*-amido-benzoic acid $C_6H_5.N_2.NH.C_6H_4.CO_2H$. Formed by mixing solutions of diazo-benzene nitrate and *m*-amido-benzoic acid (Griess, *A.* 137, 62). Small yellow plates (from ether). Sl. sol. alcohol, v. e. sol. ether.—$C_{13}H_{11}N_3O_2H_2PtCl_6$.

Ethyl ether. EtA': yellow crystals, v. e. sol. alcohol and ether.—$C_{15}H_{15}N_3O_2H_2PtCl_6$.

The above diazo-benzene-amido-benzoic acid $C_6H_5.N_2.NH.C_6H_4.CO_2H$ is identical with diazo-benzoic-acid-anilide, $C_6H_5.NH.N_2.C_6H_4.CO_2H$ (Griess, *B.* 7, 1619; *cf.* Meldola, *C. J.* 51, 435).

Diazo-benzene-anilide $Ph.N_2.NHPh$. *Diazo-amido-benzene.* Mol. w. 197. [96°].

Formation.—By passing nitrous acid gas into an alcoholic solution of aniline (Griess, *A.* 121, 258).

Preparation.—A solution of 18 pts. of sodium nitrite is added to a solution 50 pts. aniline, 15 pts. conc. H_2SO_4 in about 1,500 pts. of water, the temperature of the mixture is kept for 15 mins. between 25° and 30°, the pp. then filtered off, washed, and dried; the yield is 98 p.c. of the theoretical (Staedel a. Bauer, *B.* 19, 1952).

Properties.—Golden plates (from alcohol), or large flat prisms (from benzene). Explodes between 150° and 200°. Insol. water, and dilute acids, m. sol. cold alcohol, v. sol. hot alcohol, v. sol. ether and benzene.

Reactions.—1. Hot conc. HClAq splits it up into phenol, nitrogen, and aniline; cold HClAq gives aniline and diazobenzene chloride, which, if an excess (more than 1 mol.) of HCl is not present, recombine forming benzene-azo-aniline (*q. v.*). Unstable chlorides such as aniline hydrochloride or $ZnCl_2$ also effect the conversion into benzene-azo-aniline.—2. *Bromine* in HBrAq gives diazobenzene bromide and tribromo-aniline.—3. The hydrogen atom of the NH-group can be readily replaced by alkyl radicles by treatment with alcoholic haloids, and sodium ethylate. The alkylated diazobenzene-anilides thus obtained are split up by acids into diazo-benzene and the corresponding mono-alkyl-aniline. A proof is thus afforded of the unsymmetrical structure of the anilide, and since the only other possible formula $C_6H_5.\underset{N}{N.NH}.C_6H_5$ is excluded by the fact that the body is not reduced by alkaline reducing agents to hydrazobenzene and NH_3, the formula $Ph.N_2.NHPh$ is probably correct (Friswell a. Green, *C. J.* 49, 746; *B.* 19, 2034). 4. *Phenol* at 100° gives benzene-*p*-azo-phenol. Resorcin and the naphthols act similarly (Heumann a. Oeconomides, *B.* 20, 372).

Salts.—$Ph.N_2.NAgPh$: orange needles.—$(Ph.N_2.NHPhHCl)_2PtCl_4$: unstable crystals.

Di-sulphonamide $C_6H_4(SO_2NH_2).N_2.NH.C_6H_4.SO_2NH_2$. [183°]. Yellow needles. From $C_6H_4(SO_2NH_2)NH_2$, HNO_3 and nitrous acid gas (Hybbeneth, *A.* 221, 206). Conc. HCl converts it into $C_6H_4Cl.SO_2NH_2$, $C_6H_4(NH_2)SO_2NH_2$ and N_2.

Diazo-benzene-azo-benzene-*p*-sulphonic acid $C_6H_4(SO_3)-N_2-C_6H_4-N_2$. Small yellow needles. Nearly insoluble in most solvents. Formed by long action of nitrous acid on amido-benzene-azo-benzene-sulphonic acid. Boiled with water it gives oxy-benzene-azo-benzene-sulphonic acid; with alcohol it gives benzene-azo-benzene-sulphonic acid (Griess, *B.* 15, 2186).

Diazo-benzene-benzyl-anilide $C_6H_5.N_2.N(C_7H_7).C_6H_5$. *Benzyl-diazo-amido-benzene.* [81°]. Yellow needles. V. sol. acetone, m. sol. alcohol, insol. water.

Preparation.—30 g. of sodium are dissolved

in 800 c.c. of alcohol, a hot solution of 200 g. of diazo-benzene-anilide in 500 c.c. of absol. alcohol added, and the mixture heated with 140 g. of benzyl chloride for 1 or 2 hours; the product is precipitated by water and recrystallised from alcohol; yield, 200 g.

Reactions.—On heating it decomposes explosively. By excess of HCl it is resolved into diazobenzene and benzyl-aniline (Friswell a. Green, *B.* 19, 2036).

Diazo-benzene-bromo-anilide *v.* DIAZO-BROMO-BENZENE-ANILIDE.

Diazo - benzene-*p*-chloro - anilide. Formed from *p*-chloro-diazo-benzene and aniline. By warming with phenol it gives oxy-azo-benzene and *p* chloraniline (Heumann a. Oeconomides, *B.* 20, 908).

Diazo - benzene - ethylamide $Ph.N_2.NHEt$. From diazo-benzene nitrate and ethylamine. Picrate $C_8H_{11}N_3C_6H_2(NO_2)_3OH$.

Diazo-benzene ethyl-hydrazide $Ph.N_2.N_2H_3Et$. From diazo-benzene nitrate and ethyl hydrazine (E. Fischer, *A.* 190, 306). Very unstable oil. Reduced in alcoholic solution by zinc-dust and acetic acid to ethyl-hydrazine and phenyl-hydrazine.

Diazo-benzene-imide $C_6H_5N_3$. *Tri-azo-benzene.*

Formation. 1. Diazobenzene perbromide is treated with aqueous NH_3 and the product distilled with steam, dried over $CaCl_2$, and rectified under diminished pressure (Griess, *Tr.* 1864, iii. 700). 2. By warming nitroso-phenyl-hydrazine with dilute KOH (Fischer, *A.* 190, 92).—3. By adding Na_2CO_3 to a mixture of diazo-benzene sulphate and hydroxylamine.

Properties.—A heavy oil; insol. water, m. sol. alcohol and ether. Detonates when distilled under atmospheric pressure. Not attacked by KOH.

Reactions.—1. Reduced in alcoholic solution by Zn and H_2SO_4 to aniline and NH_3. 2. By heating with strong HCl it is converted into a mixture of *o* and *p*-chloro-aniline:

$$C_6H_5N_3 + 2HCl = C_6H_5.NH_2 + Cl_2 + N_2 = C_6H_4Cl.NH_2 + HCl + N_2.$$

3. By heating with H_2SO_4 diluted with an equal volume of water it is converted into *p*-amido-phenol: $C_6H_5N_3 + H_2O = C_6H_5.NH_2 \cdot O + N_2 = C_6H_4(OH)NH_2 + N_2$ (Griess, *B.* 19, 313).

Diazo - benzene - dimethylamide $Ph.N_2.NMe_2$. From diazobenzene nitrate and aqueous dimethylamine (Baeyer a. Jäger, *B.* 8, 893). Yellowish oil; explodes when large quantities are heated; volatile with steam; insol. water and alkalis, v. e. sol. alcohol, ether, and acids. Decomposed by acids into diazobenzene salts and dimethylamine. Aniline hydrochloride forms diazo-benzene-anilide and NMe_2H hydrochloride. Picrate $Ph.N_2.NMe_2C_6H_2(NO_2)_3(OH)$: yellow needles.

Diazo-benzene-methyl-anilide $C_6H_5.N_2.NMe.C_6H_5$. *Methyl-diazo-amido-benzene.* Heavy deep-yellow oil. Not volatile with steam. Miscible with alcohol, insol. water.

Preparation.—30 g. of sodium are dissolved in 300 c.c. of absolute alcohol and mixed with a hot solution of 200 g. diazobenzene-anilide in 500 c.c. of absolute alcohol; when nearly cold 170 g. of methyl iodide are added; a vigorous reaction soon sets in and is completed by 1 or 2 hours' cohobation; half the alcohol is then distilled off and the residue precipitated by water, the oil separated and dried over $CaCl_2$; the yield is 200 grms.

Reactions.—On heating it decomposes explosively. By excess of HCl it is resolved into diazobenzene chloride and methylaniline (Friswell a. Green, *C. J.* 49, 718; *B.* 19, 2035).

Diazo-benzene phosphonic acid nitrate (?). $NO_3.N_2.C_6H_4.PO(OH)_2$ 3aq. [188°]. S. 58 at 18°; 59 at 80°. Formed by passing nitrous acid gas into a boiling solution of amido-benzene phosphonic acid in HNO_3Aq (Michaelis a. Benzinger, *A.* 188, 288). Long white prisms (from HNO_3Aq). Explodes above 190°. V. sol. alcohol, sl. sol. ether. Not affected by boiling water, even in presence of H_2SO_4; slightly decomposed by boiling NaOHAq.

Salts.—Na_2A'' 2aq. K_2A''aq.—BaA'' 3aq.—Ag_2A''.—PbA''.

Diazo-benzene-piperidide $PhN_2NC_5H_{10}$. [43°] (Baeyer a. Jäger, *B.* 8, 893; Wallach, *A.* 235, 241).

Preparation.—Aniline (100g.) is dissolved in aqueous HCl (210 c.c.) and the solution at 0° is diazotised with $NaNO_2$ (74 g.) and then poured into a dilute aqueous solution of piperidine (100 g.) containing KOH (60 g.) cooled with ice.

Properties.—Crystals (from ether or petroleum-ether).

Reactions.—1. HCl passed into an ethereal solution gives diazobenzene chloride and piperidine hydrochloride. Aqueous HCl acts similarly. 2. Warm HCl forms N_2, chlorobenzene and piperidine hydrochloride; phenol is a by-product. HBr and HI act similarly.—3. Hot dilute H_2SO_4 forms phenol. 4. An ethereal solution of picric acid gives diazo benzene picrate.

o-Diazo-benzene sulphonic acid

$C_6H_4<\substack{SO_3\\N_2}>$ Yellowish tables, obtained by passing nitrous acid gas into water containing *o*-amido-benzene sulphonic acid in suspension (Berndsen a. Limpricht, *A.* 177, 101).

***m*-Diazo-benzene sulphonic acid**

$C_6H_4<\substack{SO_3\\N_2}>$. Prepared by passing nitrous acid gas into a concentrated solution of *m*-amido-benzene sulphonic acid, containing the free acid in suspension (Meyer a. Stuber, *A.* 165, 165; Berndsen, *A.* 177, 88). Small columns (from water). Very explosive when dry. V. sol. water and decomposed by it at 60°. Boiling HBr gives *m*-bromo-benzene sulphonic acid. Boiling alcohol has no action.

***m*-diazo-benzene sulphamide nitrate** $NO_3.N_2.C_6H_4.SO_2.NH_2$. From $C_6H_4(NH_2)SO_2NH_2$ by mixing with HNO_3 and passing in nitrous acid gas (Hybbeneth, *A.* 221, 205). Minute orange needles.

***p*-Diazo-benzene sulphonic acid**

$C_6H_4<\substack{SO_3\\N_2}>$. Formed by diazotising *p*-amido-benzene sulphonic acid (Schmitt, *A.* 120, 144; Fischer, *A.* 190, 76). Small needles (from water). Insol. cold water, v. sol. water at 60°. Boiling water forms phenol *p*-sulphonic acid. An alkaline solution gives a red colour with aldehydes (Petri, *H.* 8, 291; Zahn, *B.* 17, Ref. 290), but this is not a characteristic test for aldehydes, as

it is given also by many other bodies (E. Fischer, *B.* 16, 657; O. Loew, *J. pr.* [2] 31, 136).

Reactions.—1. *Boiling alcohol* forms benzene sulphonic acid. 2. PCl_5 at 100° has no action (Laar, *J. pr.* [2] 20, 263).

Ethyl mercaptide $C_6H_4(SO_3H).N_2.SEt$. Formed by combining *p*-diazo-benzene-sulphonic acid with an alkaline solution of ethyl mercaptan. The sodium salt (A'Na) forms yellow glistening needles, v. sol. water. It is very unstable, readily decomposing with evolution of nitrogen. When boiled with alcohol it yields ethyl-phenyl-sulphide *p*-sulphonic acid $C_2H_5.S.C_6H_4(SO_3H)$ (Stadler, *B.* 17, 2075).

Methyl anilide $C_6H_4(SO_3H).N_2.NMeC_6H_5$. Formed by combination of *p*-diazo-benzene-sulphonic acid with mono-methyl-aniline in nearly neutral solution. The sodium salt (NaA') forms large colourless plates, v. sol. water, from which it is precipitated in white felted needles by alkali; nearly insol. alcohol. Not affected by boiling with dilute caustic soda. Acids resolve it into its constituents *p*-diazo-benzene-sulphonic acid and methyl-aniline, which when the acid is dilute recombine to form methyl-amido-benzene-azo-benzene sulphonic acid $C_6H_4(SO_3H).N_2.C_6H_4.NHMe$ (Bernthsen a. Goske, *B.* 20, 926).

Piperidide $C_6H_4(SO_3H).N_2.NC_5H_{10}$ (Wallach, *A.* 235, 270). From sulphanilic acid by diazotisation and treatment with piperidine (1 mol.) and aqueous NaOH (1 mol.). Salt.—NaA': satiny plates. AgA'. Stable in neutral or alkaline solutions.

Imide $C_6H_4(SO_3H).N{<}{\overset{N}{\underset{N}{|}}}$ [1:4].

Triazo-benzene p-sulphonic acid. Formed by the action of phenyl hydrazine upon diazobenzene *p*-sulphonic acid suspended in cold water; diazobenzene-imide, sulphanilic acid, and aniline, are formed simultaneously:

$$2C_6H_4{<}\begin{matrix}N_2\\|\\SO_3\end{matrix} + 2C_6H_5NH.NH_2 =$$

$$C_6H_4(N_3)SO_3H + C_6H_5N_3 + C_6H_4(NH_2)SO_3H + C_6H_5.NH_2.$$

White deliquescent needles. V. s. sol. alcohol and water. Salts. BaA'_2 2aq: white six-sided plates, m. sol. hot water. *Phenyl hydrazine salt* $C_6H_5N_2H_4A'$aq: long white glistening plates, m. sol. hot water and alcohol, less in the cold, nearly insol. ether and chloroform; decomposed by alkalis, but not by HCl even when boiling (Griess, *B.* 20, 1528).

Diazo-benzene disulphonic acid

$C_6H_3(SO_3H){<}\begin{matrix}SO_3\\N_2\end{matrix}{>}$. The salts are formed by passing nitrous acid gas at 0° into a solution of the acid salts of $C_6H_3(NH_2)(SO_3H)_2$ [1:3:4]. The free acid is unstable (Zander, *A.* 198, 24).—KA'. BaA'_2 2aq.

Diazo-benzene disulphonic acid

$C_6H_3(SO_3H)(SO_3N_2)''$. Formed by diazotising $C_6H_3(NH_2)(SO_3H)_2$ [1:3:5]. Slender needles; v. sol. water and alcohol. Decomposed by NaOH or $BaCO_3$. The salts are formed by diazotising salts of the amido-benzene disulphonic acid (Heinzelmann, *A.* 188, 174; 190, 223).—KA'.—BaA'_2 3aq. PbA'_2 3aq.

Diazo-benzene disulphonic acid

$C_6H_3(SO_3H)(SO_3N_2)''$. Formed by diazotising $C_6H_3(NH_2)(SO_3H)_2$ [1:2:4].

Salts. — NH_4A'. — KA'. — CaA'_2 2aq. — BaA'_2 2aq.—PbA'_2 3aq (Heinzelmann a. Zander, *A.* 198, 5).

Diazo-benzene *p*-toluide is identical with diazo-toluene anilide (*q. v.*).

***o*-Diazo-benzoic acid.**

Nitrate $NO_3.N_2.C_6H_4.CO_2H$. By diazotisation of *o*-amido-benzoic acid suspended in dilute HNO_3 (Griess, *B.* 9, 1653). Colourless tables or prisms, v. e. sol. water, m. sol. alcohol. Explodes when heated. Boiling water converts it into salicylic acid. Repeated solution in water and pptn. with alcohol converts it into the so-called semi-nitrate:

$$(CO_2H.C_6H_4{<}\begin{matrix}N-N\\|\quad|\\N-N\end{matrix}{>}C_6H_4.CO_2H)HNO_3\ (?).$$

This substance is also formed by passing nitrous acid gas into an alcoholic solution of *o*-amido-benzoic acid (Griess, *A.* 117, 39; Hand, *A.* 234, 146).

Perbromide $C_7H_5N_2O_2Br_3$.

Imide $N_3.C_6H_4.CO_2H$. *Triazo-benzoic acid.* [145°]. From the perbromide and ammonia (Griess, *Z.* [2] 3, 165). Long needles. M. sol. boiling water.

***m*-Diazo-benzoic acid.**

Sulphate $SO_4H.N_2.C_6H_4.CO_2H$. Formed by passing nitrous acid gas into a thin paste of the sulphate of *m*-amido-benzoic acid; ppd. by alcohol and ether. Long white laminæ, v. e. sol. water; detonates when heated. Treatment with dilute alcohol gives rises to a 'basic sulphate' $C_7H_4N_2O_2.\frac{1}{2}H_2SO_4$ (?), or more probably $\{N_2(C_6H_4CO_2H)_2\}H_2SO_4$.

Nitrate $NO_3.N_2.C_6H_4.CO_2H$ (Griess, *A.* 120, 126). Its aqueous solution left in contact with $BaCO_3$ forms carboxy-benzene-azo-oxy-benzoic acid. With aqueous Na_2CO_3 it forms an acid $C_{21}H_{14}N_4O_7$.

Hydroxide $HO.N_2.C_6H_4.CO_2H$. Unstable yellow oil.

Chloride $Cl.N_2.C_6H_4.CO_2H$. *Combinations.*—$(ClN_2.C_6H_4.CO_2H)_2PtCl_4$: yellow prisms.—$(ClN_2.C_6H_4.CO_2H)AuCl_3$. This salt suspended in alcohol and treated with H_2S gives benzoic acid, chloro-benzoic acid, and sulphydro-benzoic acid, $HS.C_6H_4.CO_2H$ (Griess, *J. pr.* [2] 1, 102).

Perbromide $Br_3N_2.C_6H_4.CO_2H$. Oily pp. Converted by boiling alcohol into *m*-bromo-benzoic acid (Griess, *A.* 135, 121; Cunze a. Hübner, *A.* 135, 106).

Ethyl ether; nitrate. $NO_3.N_2.C_6H_4.CO_2Et$. Formed by diazotising *m*-amido-benzoic ether dissolved in nitric acid (Griess, *A.* 120, 127).—Aurochloride $(Cl.N_2.C_6H_4.CO_2Et)AuCl_3$: golden prisms (from alcohol).

Amide; nitrate. $NO_3.N_2.C_6H_4.CONH_2$. Formed by the action of nitrous acid gas on a solution of *m*-amido-benzamide in alcohol mixed with ether (Griess, *A.* 120, 127). Needles. Platinochloride $(Cl.N_2.C_6H_4.CONH_2)_2PtCl_4$.

Imide $N_3.C_6H_4.CO_2H$. *Triazobenzoic acid.* [160°]. From the perbromide and NH_3 (Griess, *Z.* 1867, 164). Thin laminæ. V. sol. alcohol and ether, m. sol. boiling water. By heating with HCl it is converted into two isomeric chloro-amido-benzoic acids, (4, 3, 1) and (2, 3, 1):

$$N_3.C_6H_4.CO_2H + 2HCl =$$
$$H_2N.C_6H_4.CO_2H + Cl_2 + N_2 =$$
$$H_2N.C_6H_3Cl.CO_2H + HCl + N_2$$

(Griess, *B.* 19, 315). Salt.—$N_3.C_6H_4.CO_2Ag$.

Anilide v. Diazo-benzene-amido-benzoic acid.

Bromo-anilide v. Diazo-bromobenzene-amido-benzoic acid.

Nitrile. Nitrate $NO_3.N_2.C_6H_4.CN$. From *m*-amido-benzonitrile (Griess, *B.* 2, 370). Explosive crystals; m. sol. cold water.—**Perbromide** $Br_3N_2.C_6H_4.CN$. Crystals.—**Imide** $N_3.C_6H_4.CN$. [57°]. Needles, v. sl. sol. water.

p-**Diazo-benzoic acid.**

Nitrate $NO_3.N_2.C_6H_4.CO_2H$. Explosive white prisms (Griess, *J.* 1864, 353).

Amide. Nitrate. $NO_3.N_2.C_6H_4.CONH_2$ (Griess, *Z.* 1866, 1).

Imide $N_3.C_6H_4.CO_2H$. *Triazobenzoic acid.* [185°]. Thin laminæ (Griess, *Z.* 1867, 164).

m-**Diazo-benzoic-*m*-amido-benzoic acid** [3:1] $CO_2H.C_6H_4.N_2.NH.C_6H_4.CO_2H$ [1:3]. Formed by passing nitrous acid gas into an alcoholic solution of *m*-amido benzoic acid, or by mixing aqueous solutions of *m*-amido-benzoic acid and the nitrate of *m*-diazo-benzoic acid (Griess, *A.* 117, 2; *Z.* 1864, 353). Orange grains. Explodes at 180°. V. sl. sol. water, alcohol, and ether. Sol. alkalis and reppd. by acids. Boiling HCl forms *m* amido-benzoic acid and *m*-chloro-benzoic acid. Bromine water gives bromo-, and tri-bromo-, benzoic acid. Boiling water and iodine form iodo-oxy-benzoic acid. Nitrous acid passed into a boiling aqueous solution forms nitro-oxy-benzoic acid; nitrous acid passed into a boiling alcoholic solution forms benzoic acid. Fuming HNO_3 gives tri-nitro-oxy-benzoic acid.

Salts. $(NH_4)_2A''$. K_2A''.—Ag_2A''.

Methyl ether Me_2A''. [160°]. Yellow needles.

Ethyl ether Et_2A''. [144°]. Golden needles.

p-**Diazo-benzoic-*p*-amido-benzoic acid** [4:1] $CO_2H.C_6H_4.N_2.NH.C_6H_4.CO_2H$ [1:4]. Orange powder, v. sl. sol. boiling alcohol. Formed by passing nitrous acid gas into an alcoholic solution of *p*-amido-benzoic acid (Beilstein a. Wilbrand, *A.* 128, 269).

m-**Diazo-benzoic-*p*-amido-benzoic acid** [3:1] $CO_2H.C_6H_4.N_2.NH.C_6H_4.CO_2H$ [1:4]. From the nitrate of *m*-diazo-benzoic acid and *p* amido-benzoic acid (Griess, *J.* 1864, 353). An isomeric (?) acid is got from the nitrate of *p*-diazo-benzoic acid and *m*-amido-benzoic acid.

m-**Diazo-bromo-benzene.**

Perbromide $C_6H_4Br.N_2Br_3$ (Wurster, *A.* 176, 173).

p-**Diazo-bromo-benzene.**

Nitrate $C_6H_4Br.N_2.NO_3$. Formed by passing nitrous acid gas into an aqueous solution of *p*-bromo-aniline nitrate (Griess, *Tr.* 1864, iii. 695). Ppd. by alcohol and ether.

Hydroxide $C_6H_4Br.N_2.OH$: bright yellow needles. Very explosive.—$C_6H_4Br.N_2.OK$. From the nitrate and strong KOH; gives the preceding body when treated with acetic acid.—$C_6H_4Br.N_2OAg$.

Bromide $C_6H_4Br.N_2Br$: scales; v. sol. water, m. sol. alcohol, insol. ether. $(C_6H_4Br.N_2Br)_2PtBr_4$.

Perbromide $C_6H_4Br.N_2Br_3$: monoclinic prisms (from alcohol), v. sl. sol. ether, insol. water.

Chloride $C_6H_4Br.N_2Cl$: from the bromide and moist silver chloride.—$(C_6H_4Br.N_2Cl)AuCl_3$.—$(C_6H_4Br.N_2Cl)_2PtCl_4$.

Sulphate $C_6H_4Br.N_2.SO_4H$: slender prisms.

Imide $C_6H_4Br.N_3$. *Triazo-bromo-benzene.* [20°]. Insol. water, m. sol. alcohol, v. sol. ether and benzene. Reduced by Zn and H_2SO_4 to bromo-aniline and NH_3.

Cyanide $C_6H_4Br.N_2.CNHCN$. [128°]. From *p*-diazo-bromo-benzene nitrate and aqueous KCN (Gabriel, *B.* 12, 1638).

Anilide $C_6H_4Br.N_2.NH.C_6H_5$ or, alternatively $C_6H_5.N_2.NH.C_6H_4Br$. Formed either from diazo benzene nitrate and *p* bromo-aniline or from *p*-diazo-bromo-benzene nitrate and aniline (Griess, *B.* 7, 1618). Yellow plates; v. e. sol. ether, m. sol. alcohol. $(C_{12}H_{10}BrN_3HCl)_2PtCl_4$.

p-Bromo-anilide $C_6H_4Br.N_2.NH.C_6H_4Br$. [145°]. Obtained from *p*-bromo-aniline.—$(C_{12}H_9Br_2N_3)_2H_2PtCl_6$.

Diazo di-bromo-benzene.

Nitrate $C_6H_3Br_2.N_2.NO_3$ [2:4:1]. Obtained by passing nitrous acid into an aqueous solution of the nitrate of di-bromo-aniline (Griess, *Tr.* 1864, iii. 701). Needles or plates.

Platinochloride $(C_6H_3Br_2.N_2Cl)_2PtCl_4$: orange plates.

Perbromide $C_6H_3Br_2.N_2Br_3$: slender needles.

Imide $C_6H_3Br_2.N_3$. [62°]: needles.

Di-bromo-anilide $C_6H_3Br_2.N_2.NHC_6H_3Br_2$. [168°]. From (2, 4, 1)-di bromo aniline. Golden needles, v. sl. sol. alcohol and ether.

Diazo-tri bromo-benzene.

Nitrate $C_6H_2Br_3.N_2.NO_3$ [2:4:6:1]. Formed when a *rapid* current of nitrous acid gas is passed into alcohol containing tri-bromo-aniline in suspension together with excess of HNO_3. As soon as everything is dissolved, ether is added and a bright yellow crystalline pp. of the diazo-nitrate is formed (H. Silberstein, *J. pr.* [2] 27, 102).

Properties.—Yellow trimetric plates. Explodes at 85°. Sol. water and HCl. V. sl. sol. alcohol, ether, and benzene.

Reactions.—1. Boiled with *alcohol* it gives tri-bromo-benzene, N_2, HNO_3 and aldehyde.—2. Boiled with *water*, gives off no nitrogen but forms undetermined compounds.—3. Heated with glacial *acetic acid* gives off N_2 and nitrous fumes and leaves tri-bromo-benzene. 4. Heated with *benzene* (4 pts.) it decomposes at 45° forming a diazo-di-bromo-phenol (*q. v.*), tetra-bromo-benzene [98°], and nitrobenzene.—5. Heated with $CHCl_3$ it gives diazo-di-bromo-phenol and tetra-bromo-benzene. 6. Heated with concentrated HCl it forms crystals of the *perbromide* of diazo-tri bromo-benzene chloride, $C_6H_2Br_3N_2ClBr_2$. Probably chlorine, liberated in this reaction, turns out bromine from some of the tri-bromo-compound, which bromine then unites with the diazo-chloride. The perbromide explodes at 100°, forming chloro-tri-bromo-benzene.—7. With HBr it gives the bromide (*q. v.*).—8. With HI it gives tri-bromo-iodo-benzene.

Sulphate $C_6H_2Br_3N_2.SO_4H$.

Properties.—Colourless prisms. Sol. water, sl. sol. alcohol, insol. ether and benzene.

Reactions.—1. Decomposed by *alcohol* into tri-bromo-benzene, H_2SO_4 and N_2. 2. Boiled with acidulated *water* it forms no tri-bromo-phenol.—3. Heated with glacial *acetic acid* it forms tri-bromo-benzene.—4. Not affected by boiling *benzene*.

Bromide $C_6H_2Br_3N_2Br$. Small golden tri-

metric tablets, got by adding dilute HBr to a solution of the nitrate. Decomposed by sunlight into N_2 and $C_6H_2Br_4$. Sl. sol. water, insol. alcohol and ether. Heated with glacial *acetic acid* it gives unsymmetrical $C_6H_2Br_4$.

Perbromide $C_6H_2Br_4N_2Br_2$. Formed by adding conc. HBr to a solution of the nitrate, $C_6H_2Br_3N_2NO_3$; the liquid is filtered from $C_6H_2Br_3N_2Br$ and evaporated to crystallisation. It forms orange prisms and behaves very much like $C_6H_2Br_3N_2ClBr_2$ (*q. v.*).

Chloro-perbromide $C_6H_2Br_3N_2Cl.Br_2$. From tri-bromo-diazo-benzene nitrate (*q. v.*) and HCl. It explodes at 100° forming chloro-tri-bromo-benzene. *Reactions.*—1. With NH_3 gives tri-bromo-diazo-benzene imide (*q. v.*).—2. With alcoholic *dimethylaniline* forms tri-bromo-benzene-azo-dimethylaniline $C_6H_2Br_3.N_2.C_6H_4NMe_2$. 3. With alcoholic *methyl-di-phenylamine* it forms tri-bromo-benzene-azo-methyl-di-phenyl-amine $C_6H_2Br_3N_2.C_6H_4NMePh$.—4. With *mercuric diphenyl* it forms chloro-tri-bromo-benzene and nitrogen (Silberstein, *J. pr.* [2] 27, 117).

Imide $C_6H_2Br_3.N_3$. [59°]. Formed by adding dilute ammonia to $C_6H_2Br_3N_2ClBr_2$. Colourless needles. May be distilled with steam. Insol. water, sol. warm alcohol, ether, and $CHCl_3$. Unlike diazo benzene-imide, it is not reduced by Zn and H_2SO_4 to NH_3 and tri-bromo-aniline (Silberstein, *J. pr.* [2] 27, 116).

Anilide $C_6H_2Br_3N_2NHPh$. [101°]. From alcoholic aniline (2 mols.) and $C_6H_2Br_3N_2NO_3$ (1 mol.). The pp. is crystallised from alcohol (Silberstein, *J. pr.* [2] 27, 121). Yellow, glittering, triclinic prisms. Insol. water, sol. hot alcohol, ether, and benzene. Boiled with glacial acetic acid it gives nitrogen and tri-bromo-aniline.

Tri-bromo-anilide
$C_6H_2Br_3.N_2.NH.C_6H_2Br_3$. Obtained by passing N_2O_3 slowly into a cold alcoholic solution of tri-bromaniline. Some $C_6H_2Br_3N_2NO_3$ is formed at the same time. The product is washed with water and hot alcohol and crystallised from benzene. The yield is bad (Silberstein, *J. pr.* [2] 27, 120). Insol. water and alcohol, v. sl. sol. ether. V. sol. $CHCl_3$ and benzene. Not attacked by cold acids, but decomposed by boiling with acids with evolution of N_2.

Diazo-*p*-bromo-benzene-amido-benzoic acid
$C_6H_4Br.N_2.NH.C_6H_4.CO_2H$. *Diazo-benzoic acid p-bromo-anilide.* From *p*-diazo-bromo-benzene nitrate and *m*-amido-benzoic acid (Griess, *J.* 1866, 453). Clusters of needles.

Diazo-bromo-benzene sulphonic acid

$C_6H_3Br<\substack{SO_3\\N_2}>$ $\left[4\ \substack{2\\1}\right]$. From the corresponding bromo-amido-sulphonic acid (Borns, *A.* 187, 371). Small yellow needles, v. sol. water, m. sol. alcohol; explodes when struck or when heated. Heated with alcohol, it gives *m*-bromo-benzene sulphonic acid. Conc. HBr gives $C_6H_3Br_2(SO_3H)$ [4:1:2].

Diazo-bromo-benzene disulphonic acid

$$C_6H_2Br(SO_3H)<\substack{SO_3\\N_2}>.$$

From $C_6H_2(NH_2)(SO_3H)_2Br$ [1:4:6:2]. Minute plates; v. sol. water and alcohol. Does not explode when struck (Zander, *A.* 198, 15).—KA' 3aq.

[illegible]

$C_6H_2Br_2<\substack{SO_3\\N_2}>$. From $C_6H_2(NH_2)Br_2(SO_3H)$ [1:2:6:4]. Yellowish scales; explodes above 100°. V. sl. sol. cold water, v. sol. hot water. Boiling water gives di-bromo-phenol sulphonic acid. Heated with alcohol it gives di-bromo-benzene sulphonic acid.

Diazo-di-bromo-benzene-sulphonic-acid-di-bromo-sulphanilide

$C_6H_2Br_2(SO_3H).N_2.NH.C_6H_2Br_2(SO_3H)$. [70°–80°]. From $C_6H_2Br_2(NH_2)SO_3H$ [2:4:1:5] by warming with alcohol and KNO_2. Needles (from water). Insol. alcohol (Baessmann, *A* 191, 229).

Diazo-di-bromo-benzene-disulphonic acid

$C_6HBr_2(SO_3H)<\substack{SO_3\\N_2}>$. From the nitro-benzene disulphonic acid [1:3:5]? whose chloride melts at 96°, by reduction, bromination and diazotisation (Heinzelmann, *A.* 188, 183).

Diazo-tri-bromo-benzene sulphonic acid

$C_6HBr_3<\substack{SO_3\\N_2}>$. From tri-bromo-aniline, $C_6H_2(NH_2)Br_3$ [1:3:4:5] by sulphonation and diazotisation (Spiegelberg, *A.* 197, 291). Minute needles.

Diazo-tetra-bromo-benzene *p*-sulphonic acid

$C_6Br_4<\substack{SO_3\\N_2}>$. Crystalline powder not decomposed by boiling alcohol (Beckurts, *A.* 131, 225).

Diazo-bromo-nitro-toluene sulphonic acid

$C_6HMeBr(NO_2)<\substack{N_2\\SO_3}>$. Formed by projecting *m*-bromo-*p*-amido-toluene *o*-sulphonic acid into fuming HNO_3 (Weckwarth, *A.* 172, 203).

Diazo-di-bromo-nitro-toluene sulphonic acid

$C_6Br_2Me(NO_2)<\substack{N_2\\SO_3}>$. Formed by projecting di-bromo-*o*-amido-toluene *p*-sulphonic acid into fuming HNO_3 (Hayduck, *A.* 174, 355).

Diazo-di-bromo-phenol

$C_6H_2Br_2<\substack{O\\N_2}>$ [$O:N_2 = 1:2$].

Preparation.—Bromine water is added to an aqueous solution of *o*-diazo-phenol chloride and the pp. is dissolved in fuming HCl, filtered through asbestos and ppd. by water.

Properties.—Orange crystalline powder, much less stable than the *p*- compound. When heated it explodes at 128°. It is more soluble in cold water than the *p*- compound; on warming the solution a resin is formed. The solution gives an amorphous grey pp. with silver nitrate. It is almost insoluble in alcohol, ether and CS_2, but readily dissolves in $CHCl_3$, hot benzene, and benzoline. It does not reduce Fehling's solution, nor form a crystalline body with $NaHSO_3$. $C_6H_2Br_2(OH)N_2Br\,1\tfrac{1}{2}aq$: decomposed by water.

Ethyl ether, nitrate of.
$C_6H_2Br_2(OEt).N_2NO_3$. Got by passing N_2O_3 into alcohol containing HNO_3 and di-bromo-*o*-amido-phenetol in suspension, and pouring it into dry ether at 0°. *Properties.*—Prisms. Explodes at 102°. If its alcoholic solution be diluted with water (10 vols.) and boiled as long as N_2 escapes, it is converted into di-bromo-phenetol, bromine being replaced by hydrogen, not by hydroxyl (Möhlau a. Oehmichen, *J. pr.* [2] 24, 482).

Diazo-di-bromo-phenol

$C_6H_2Br_2<\begin{matrix}O\\N_2\end{matrix}>$. [$O:N_2 = 1:4$].

Formation.—1. Obtained by adding bromine water to an aqueous solution of any salt of *p*-diazo-phenol: $C_6H_4(OH)N_2Cl + 2Br_2 = C_6H_2Br_2<\begin{matrix}O\\N_2\end{matrix} + HCl + 2HBr$.—2. From HBr and diazophenol nitrate (*q. v.*).

Properties. — A flocculent yellow pp. resembling sulphide of arsenic. Dissolves in boiling water, without decomposition, and crystallises in yellow prisms as the solution cools. Almost insoluble in cold water, ether, and CS_2, somewhat more soluble in $CHCl_3$. Soluble in alcohol and in amyl alcohol. May be kept for months in closed bottles in the dark, but, when exposed to air and light, it soon turns brown. Heated to 137° it explodes.

Salts. — Unstable, decomposed by water and by alcohol. $C_6H_2Br_2(OH)N_2Br$, aq. — $\{C_6H_2Br_2(OH)N_2Br\}_2PtCl_4$: triclinic plates, decomposed by water. — $C_6H_2Br_2(OH)N_2SO_4H$ (Böhmer, *J. pr.* 132, 458).

Reactions.—1. Boiled with *water* of which the boiling-point, by addition of calcic chloride, has been raised to 120°, it gives off nitrogen and forms di-bromo-hydroquinone:

$$C_6H_2Br_2<\begin{matrix}O\\N_2\end{matrix} + H_2O = C_6H_2Br_2<\begin{matrix}OH\\OH\end{matrix} + N_2$$

(Böhmer, *J. pr.* 132, 464).—2. Dissolves in a hot solution of $NaHSO_3$; and as the solution cools, yellow needles of $C_6H_2Br_2(OH)N_2SO_3Na\,2aq$ are formed. These crystals dissolve in ether, benzene and CS_2; do not explode when heated; show Liebermann's reaction; do not reduce Fehling's solution; and give with $BaCl_2$ golden scales of $\{C_6H_2Br_2(OH)N_2SO_3\}_2Ba\,5aq$.—3. Reduced by Sn and HCl to di-bromo-*p*-amido-phenol.

Diazo-di-bromo-phenol. (?) Identical with the preceding diazo-di-bromo-phenol just described may be converted into this isomeride by first reducing it to dibromo-*p*-amido-phenol hydrochloride and again diazotising.

Properties.—Explodes at 145°, has a greyish-yellow colour, is insoluble in water. Crystallises from alcohol in much thinner needles than the preceding. With $NaHSO_3$ it forms small plates, whereas the sulphonate of its parent-isomeride crystallises in needles (Böhmer, *J. pr.* 132, 471).

Diazo-di-bromo-phenol

$C_6H_2Br_2<\begin{matrix}N_2\\O\end{matrix}>$. [$Br:Br:N:O = 1:5:6:3$]. Formed by heating tri-bromo-diazo-benzene nitrate with benzene at 45° (Silberstein, *J. pr.* [2] 27, 107).

Properties.—Oblique prisms, from water. Crystallises from alcohol. Explodes at 142°. Soluble in hot alcohol. Nearly insoluble in chloroform and ether.

Salts.—These are very unstable; they are formed by warming with rather strong solutions of acids, but are saponified by water.

Reactions.—1. Not attacked by boiling *water*. 2. Heated with strong HBr forms tri-bromo-phenol and N_2.—3. Reduced by Sn and HCl to di-bromo-amido-phenol and NH_3.

Constitution.—The hydrochloride of the di-bromo-amido-phenol obtained by reduction, gives Schmitt's reaction upon the gradual addition of dilute bleaching powder, viz.: a violet colour followed by a white pp. As this reaction is characteristic of *p*-amido-phenols, this body must be di-bromo-*p*-amido-phenol, and since it is formed from $C_6H_2(NH_2)Br_3$ [1:2:4:6] its constitution is as given above. It appears to be different from Böhmer's compound, exploding at 137°.

Diazo-tri-bromo-phenol.

Ethyl ether, nitrate of. $C_6HBr_3(OEt)N_2NO_3$[$OEt:N_2 = 1:2$]. Triclinic plates, prepared by bromination of *o*-diazo-phenetol. Does not explode when struck. In melting-point tubes it explodes at 93°. It is decomposed by boiling water into tri-bromo-phenetol, the N_2NO_3 being displaced by H, not by OH (Möhlau a. Oehmichen, *J. pr.* 132, 484):

$$2C_6HBr_3(OEt)N_2NO_3 + 2H_2O = 2C_6HBr_3(OEt)H + 2N_2 + O_2 + 2HNO_3.$$

Diazo-bromo-toluene sulphonic acids

$CH_3.C_6H_2Br<\begin{matrix}N_2\\SO_3\end{matrix}>$. Five are known:

p-**diazo-*m*-bromo-toluene *o*-sulphonic acid** (Weckwarth, *A.* 172, 196). Red crystals. Heated with alcohol under pressure it gives bromo-toluene sulphonic acid.

p-**diazo-bromo-toluene *m*-sulphonic acid** (Pechmann, *A.* 173, 211). Heated with alcohol under pressure it gives bromo-toluene *m*-sulphonic acid.

diazo-*o*-bromo-toluene *m*-sulphonic acid (Schäfer, *A.* 174, 360).

diazo-*p*-bromo-toluene *m*-sulphonic acid (S.).

diazo-*p*-bromo-toluene *o*-sulphonic acid (S.).

o-**Diazo-di-bromo-toluene *p*-sulphonic acid** (Hayduck, *A.* 174, 352).

Diazo-camphor v. CAMPHOR.

Diazo-*p*-chloro-benzene [1:4] $C_6H_4Cl.N_2.OH$. Yellow explosive powder, ppd. from its salts by HOAc. **Salts.**—$C_6H_4Cl.N_2.NO_3$: white plates.—$C_6H_4Cl.N_2Br_3$: yellow prisms.—$C_6H_4Cl.N_2$.—$(C_6H_4ClN_2Cl)_2PtCl_4$ (Griess, *Tr.* 1864, iii. 705).

Anilide v. Diazo-benzene *p*-chloro-anilide.

p-Chloro-anilide $C_6H_4Cl.N_2.NH.C_6H_4Cl$ [125°].

Diazo-di-chloro-benzene.

Salts. — $C_6H_3Cl_2.N_2NO_3$. — $C_6H_3Cl_2.N_2Br_3$.—$(C_6H_3Cl_2.N_2Cl)_2PtCl_4$ (G.).

Di-chloro-anilide $C_6H_3Cl_2.N_2.NH.C_6H_3Cl_2$ [127°]. Needles, v. sl. sol. alcohol and ether.

Diazo-chloro-nitro-phenol

$C_6H_2Cl(NO_2)<\begin{matrix}N_2\\O\end{matrix}>$. From chloro-nitro-amido-phenol (Griess, *A.* 113, 215). Brownish-red columns (from alcohol).

Diazo-di-chloro-phenol $C_6H_2Cl_2<\begin{matrix}N_2\\O\end{matrix}>$. From $C_6H_2(OH)Cl_2(NH_2)$ [1:3:5:2] (Schmitt a. Glutz, *B.* 2, 52). Brown flocculent powder.

Diazo-tri-chloro-phenol $C_6HCl_3<\begin{matrix}N_2\\O\end{matrix}>$. From tri-chloro-*p*-amido-phenol (Lampert, *J. pr.* [2] 33, 375). Golden needles, explodes at 187°. Sl. sol. hot alcohol or benzene, insol. ether.

Reactions.—1. Boiling alcohol gives a tri-chloro-phenol [54°] (253°).—2. Conc. Na_2SO_3Aq forms $C_6HCl_3(ONa).N_2SO_3Na$, of which the acid $C_6HCl_3(OH).N_2.SO_3H$, explodes at 200°, and forms an orange crystalline barium salt.—3. HI forms $C_6HCl_3I.OH$.

Diazo-chloro-thymol chloride

$C_6HClMePr(OH).N_2Cl$. By the action of N_2O_3 on

a cold alcoholic solution of hydrochloride of chloro-amido-thymol (Andresen, *J. pr.* 131, 180). Precipitated by ether. Colourless needles, often grouped in fans.

o-**Diazo-cinnamic acid.** From amido-cinnamic acid (10 pts.), HCl (9 pts. of S.G. 1·19), water (70 pts.), and $NaNO_2$. The *chloride* separates as a yellow powder (Fischer a. Kuzel, *B.* 14, 478; *A.* 221, 272). The *nitrate* $C_6H_4(N_2NO_3).CH{:}CH.CO_2H$ forms clear prisms. Both salts may be boiled with potash without giving off nitrogen, but they are decomposed by boiling water, forming *o*-coumaric acid. With Na_2SO_3 they form $C_6H_4(N_2SO_3Na).CH{:}CH.CO_2H$, whence, by reducing with zinc and HCl, $C_6H_4(NH.NH.SO_3Na).CH{:}CH.CO_2H$. The latter forms slender needles. It reduces HgO in the cold, and Fehling's solution. HCl in the cold converts it into hydrazido-cinnamic acid (*q. v.*).

p-**Diazo-cinnamic acid.** The *chloride* $C_6H_4(N{:}N.Cl).CH{:}CH.CO_2H$ is prepared by the action of $NaNO_2$ on *p*-amido-cinnamic acid suspended in HCl (Gabriel, *B.* 15, 2300). Long needles (containing aq). M. sol. water. Can be dried at a gentle heat without decomposition.

p-**Diazo-cresol** $Me.C_6H_3\left\langle\begin{matrix}N_2\\O\end{matrix}\right\rangle$. Formed by diazotising $C_6H_3Me(NH_2)(OH)$ [1:3:4] (Wagner, *B.* 7, 1270).—$(MeC_6H_3(OH)N_2Cl)_2PtCl_4$: powder, m. sol. water.

Diazo-ψ-cumene-sulphite.

Salt.—$C_6H_2(CH_3)_3.N_2.SO_3Na$ [1:3:4:6]. Transparent prisms (containing 2½ aq). Not explosive (Haller, *B.* 18, 90).

Diazo-ψ-cumene-cumide. *Diazoamidocumene.* [1:3:4:6] $C_6H_2Me_3.N{:}N.NH.C_6H_2Me_3$ [6:1:3:4]. [131°]. Formed by the combination of diazo-cumene with cumidine (Nölting a. Baumann, *B.* 18, 1147). Yellow tables (from ether). V. sol. benzene, ether, and acetone, m. sol. alcohol.

Diazo-cuminic-amido-cuminic acid $Pr.C_6H_3(CO_2H).N_2.NH.C_6H_3Pr.CO_2H$. Formed by passing nitrous acid into an alcoholic solution of amido-cuminic acid at 0°. Minute prisms or leaflets (Griess, *A.* 117, 62).

Diazo-ethane sulphite $C_2H_5.N_2.SO_3H$. *Diazo-ethane sulphonic acid.*

Salt.—KA'. Formed by the action of HgO on the corresponding hydrazo- derivative $C_2H_5.NH.NH.SO_3K$ (Fischer, *A.* 199, 302). V. sol. water; ppd. by alcohol. Explodes when heated. Decomposed by boiling acids, N_2 and SO_2 coming off. Reduced by zinc-dust and acetic acid to $C_2H_5.NH.NH.SO_3K$.

Diazo-ethoxane $C_2H_5.O{-}N_2{-}O.C_2H_5$ (?) V.D. 4·02 (calc. 4·08). Prepared by the action of silver hyponitrite, AgNO, on EtI (Zorn, *B.* 11, 1630). Neutral liquid. Exceedingly explosive. Is decomposed by water with production of aldehyde and alcohol: $(C_2H_5)_2O_2N_2 + H_2O = N_2 + CH_3.COH + C_2H_5OH + H_2O$. By tin and acetic acid it is reduced to nitrogen and alcohol: $(C_2H_5)_2O_2N_2 + H_2 = 2C_2H_5OH + N_2$.

o-**Diazo-hemipic acid**

$C_6H(OMe)_2(CO_2H)\left\langle\begin{matrix}N_2\\CO\end{matrix}\right\rangle O$. *Diazo-di-methoxy-phthalic acid.* Formed by the action of nitrous acid upon *o*-amido-hemipic acid. Yellow micro-crystalline powder. Sl. sol. ordinary solvents. Explodes on percussion or when heated to 140°–150°. Converted into hemipic acid by boiling with alcohol.

Hydrochloride $C_6H(OMe)_2(CO_2H)_2.N_2Cl aq$: long colourless needles.

The *sulphate* forms small prisms (Grüne, *B.* 19, 2302).

Diazo-hippuric acid.

The *nitrate* $CO_2H.CH_2.NH.CO.C_6H_4.N_2.NO_3$ is formed by diazotising the nitrate of *m*-amido-hippuric acid (Griess, *Z.* 1867, 165).—*Perbromide* $C_9H_8NO_3.N_2Br_3$: yellow prisms. *Imide* $C_9H_8NO_3.N_3$: tables or needles.

Diazo-leucaniline *v.* Hexa-azo-tri-phenyl-methane (*infra*).

p-**Diazo-iodo-benzene** $C_6H_4I.N_2OH$: yellow pp.

Salts.—$(C_6H_4I.N_2Cl)_2PtCl_4$.—$C_6H_4I.N_2NO_3$.—$C_6H_4I.N_2SO_4H$: small plates, v. sol. water, sl. sol. alcohol.—$C_6H_4I.N_2Br_3$.—*Imide* $C_6H_4I.N_3$ (Griess, *Tr.* 1864, iii. 706).

(*α*)-**Diazo-naphthalene** (Griess, *J.* 1866, 453). *Nitrate* $C_{10}H_7.N_2.NO_3$: formed by diazotising *α*-naphthylamine nitrate. — *Perbromide* $C_{10}H_7.N_2Br_3$: orange crystals.—*Platinochloride* $(C_{10}H_7.N_2Cl)_2PtCl_4$.—*Imide* $C_{10}H_7.N_3$: yellowish oil (*cf.* Fischer, *A.* 232, 242).

A solution of the chloride neutralised by Na_2CO_3 gives a brown pp. Part of this dissolves in alkalis and appears to be $C_{10}H_7NO$, the rest is ppd. as minute crystals by adding alcohol to its benzene solution. Analysis indicates $C_{30}H_{23}N_5O_2$. Both form crimson solutions in alcohol, ether, benzene, and glacial acetic acid (P. F. Frankland, *C. J.* 37, 750).

(*β*)-**Diazo-naphthalene.** Obtained by diazotising (*β*)-naphthylamine (Liebermann a. Palm, *A.* 183, 267). The *sulphate* forms pale yellow needles, and the *perbromide* orange needles.

$(C_{10}H_7.N_2.Cl)Cu_2Cl_2$*: very unstable yellow pp. which is formed on adding Cu_2Cl_2 to a cold solution of *β*-diazo-naphthalene-chloride. $(C_{10}H_7.N_2.Br)Cu_2Br_2$: red pp.; on boiling with water it evolves nitrogen yielding (*β*)-bromo-naphthalene (Lellmann, *B.* 19, 810).

(*α*)-**Diazo-naphthalene-(*α*)-naphthylamide.** [100°]. Formed by action of nitrous acid on (*α*)-naphthylamine, or by ppg. a solution of (*α*)-diazo-naphthalene chloride with (*α*)-naphthylamine. Brown laminæ (from alcohol). Acids resolve it into naphthylamine and diazo-naphthalene (Martius, *Z.* [2] 2, 137).

(*α*)-**Diazo-naphthalene sulphonic acid**

*$C_{10}H_6\left\langle\begin{matrix}N{:}N\\SO_3\end{matrix}\right\rangle$. [1:4]. Got by passing nitrous acid gas into (*α*)-naphthylamine sulphonic acid (formed by sulphonating (*α*)-naphthylamine) suspended in water (Clève, *Bl.* [2] 26, 241; Nevile a. Winther, *C. J.* 37, 632). Powder, nearly insoluble in cold water. Boiling water converts it into a crimson dye, forming very little naphthol sulphonic acid. Heated with dilute H_2SO_4 (*α*)-naphthol *p*-sulphonic acid is formed. By heating with strong H_2SO_4, or with water at 160°, (*α*)-naphthol is produced. Dilute HNO_3 (7 to 15 p.c. HNO_3) forms di-nitro-naphthol, [138°]. Conc. HCl forms a chloro-naphthalene sulphonic acid, whence PCl_5 forms dichloro-naphthalene [68°].

Imide $C_{10}H_6(SO_3H).N\left\langle\begin{matrix}N\\N\end{matrix}\right.$ [1:4].

Triazo-naphthalene-p-sulphonic acid. Formed by the action of phenyl-hydrazine upon the

acid; diazo-benzene-imide, (a)-naphthylamine-p-sulphonic acid, and aniline are formed simultaneously: $2C_{10}H_6\left<\begin{matrix}N_2\\|\\SO_3\end{matrix}\right. + 2C_6H_5NH.NH_2 =$

$C_{10}H_6(N_3)SO_3H + C_6H_5N_3 + C_{10}H_6(NH_2)SO_3H + C_6H_5.NH_2$. White needles. V. sol. water and alcohol.

Salt.—BaA'_2: white silvery plates, v. sl. sol. boiling water. **Phenyl-hydrazine salt** $C_6H_5N_2H_4A'$: long plates; v. sol. alcohol, nearly insol. ether and chloroform (Griess, *B.* 20, 1530).

(a)-Diazo-naphthalene sulphonic acid $C_{10}H_6<^{N_2}_{SO_3}>$. [1:1' or 4']. Similarly prepared from the product of the reduction of (a)-nitro-(a)-naphthalene sulphonic acid formed by sulphonating nitro-naphthalene (Clève, *Bl.* [2] 24, 512). Yellow crystalline powder. Boiling water gives (?)-naphthol (a)-sulphonic acid.

(β)-Diazo-naphthalene sulphonic acid $C_{10}H_6<^{N_2}_{SO_3}>$. Microcrystalline powder. Formed by diazotising (β)-naphthylamine sulphonic acid (formed by sulphonating (β)-naphthylamine). By boiling with HCl, converting into the K salt and heating with PCl_5 it yields chloro-naphthalene-sulphonic chloride [129°] (Forsling, *B.* 19, 1715).

(β)-Diazo-naphthalene sulphonic acid $C_{10}H_6<^{N_2}_{SO_3}>$. Formed by diazotising (?$\beta_1\beta_2$)-naphthylamine sulphonic acid, itself got by the action of NH_3 upon Schäffer's (β)-naphthol sulphonic acid at 180°. Minute crystals. Converted by treatment with cuprous chloride into (β)-chloro naphthalene sulphonic acid, whose chloride melts at 110°, and, by distillation with PCl_5 is converted into (ε)-di-chloro-naphthalene, [136°] (Forsling, *B.* 20, 80).

Tetrazo-dinaphthyl $HO.N_2.C_{10}H_6.C_{10}H_6.N_2OH$. Formed by diazotising naphthidine. It gives violet dye-stuffs when combined with the sulphonic acids of (β)-naphthol. By boiling with alcohol it yields (aa)-dinaphthyl.

Salts.—$C_{20}H_{12}N_4SO_4$*: yellowish plates.—$(C_{20}H_{12}N_4Cl_2)PtCl_4$: sparingly soluble yellow needles (Nietzki a. Goll, *B.* 18, 3256).

Diazo-nitro-benzaldoxim chloride $C_6H_3(NO_2)(N:NCl)(CH:NOH)$ [3:4:1]. Formed by the action of amyl nitrite and HCl on (3:4:1)-nitro-amido-phenyl-acetic acid (Gabriel, *B.* 15, 837). Plates or needles. Explodes on heating. On heating with alcohol it gives *m*-nitro-benzaldoxim $C_6H_4(NO_2)(CH:NOH)$.

***p*-Diazo-*o*-nitro-benzaldoxim chloride** $C_6H_3(NO_2)(N_2Cl)(CH:NOH)$ [2:4:1]. Formed, with evolution of CO_2, by the action of amyl nitrite on a HCl solution of *o*-nitro-*p*-amido-phenyl-acetic acid (Gabriel a. R. Meyer, *B.* 14, 826; *C. C.* 1885, 516). Long red needles. Explosive. By the action of HBr it gives *o*-nitro-*p*-bromo-benzaldoxim. By hot alcohol it gives *o*-nitro-benzaldoxim $C_6H_4(NO_2)(CH:NOH)$. On oxidation it gives *o*-nitro-benzaldehyde. Ammonium sulphide reduces it to *o*-amido-benzaldoxim $C_6H_4(NH_2).CH:NOH$ [133°].

***m*-Diazo-nitro-benzene.** Formed by diazotising *m*-nitro-aniline.

Nitrate $C_6H_4(NO_2).N_2.NO_3$: cubes.—$(C_6H_4(NO_2).N_2Cl)_2PtCl_4$.—$C_6H_4(NO_2).N_2Br_3$ (Griess, *Tr.* 1864, iii. 708).

Imide $C_6H_4(NO_2).N_3$. [52°].

***p*-Diazo-nitro-benzene.** Formed by diazotising *p*-nitro-aniline.

Nitrate $C_6H_4(NO_2).N_2.NO_3$: slender needles. Gives no pp. with $PtCl_4$.

Imide $C_6H_4(NO_2).N_3$. [71°].

***m*-Diazo-nitro-benzene-*p*-ethyl-toluide** [3:1] $C_6H_4(NO_2)-N_2-NEt.C_6H_4Me$ [1:4]. [55°]. From *m*-diazo-nitro-benzene chloride and ethyl-*p*-toluidine (Gastiger, *Bl.* [2] 42, 312). Resolved by dilute HCl into its generators.

***p*-Diazo-nitro-benzene-*p*-ethyl-toluide** [4:1] $C_6H_4(NO_2)-N_2-NEt.C_6H_4Me$ [1:4]. [105°]. Yellow needles (Gastiger, *Bl.* [2] 42, 312). Resolved by HCl into *p*-diazo-nitro-benzene chloride and ethyl-*p*-toluidine.

***m*-Diazo-nitro-benzene-*m*-nitro-anilide** [3:1] $C_6H_4(NO_2).N_2.NH.C_6H_4(NO_2)$ [1:3]. [195°]. Formed by the action of nitrous acid (1 mol.) on *m*-nitro-aniline (2 mols.). Small red prisms, v. sl. sol. alcohol (Griess, *A.* 121, 272; Meldola a. Streatfeild, *C. J.* 51, 107). Insol. hot aqueous KOH; but the potassium salt separates as brown crystals from a solution in alcoholic KOH. Cold HClAq gives *m*-nitro-aniline and *m*-diazo-nitro-benzene chloride.

***p*-Diazo-nitro-benzene-*p*-nitro-anilide** [4:1] $C_6H_4(NO_2).N_2.NH.C_6H_4(NO_2)$ [1:4]. [223°]. Formed by the action of nitrous acid (1 mol.) on *p*-nitro-aniline (2 mols.) (Griess, *A.* 121, 271; Meldola a. Streatfeild, *C. J.* 49, 624). Small yellow needles, m. sol. boiling alcohol. Possesses distinctly acid properties, decomposing Na_2CO_3. Cold alcoholic KOH or boiling aqueous KOH form a magenta-coloured solution of the potassium salt. It forms *p*-nitro-aniline when heated with dilute H_2SO_4 or with water in sealed tubes at 230°. Conc. HCl at 20° gives *p*-diazo-nitro-benzene chloride and *p*-nitro-aniline.

Salts.—$C_6H_4(NO_2).N_2.NNa.C_6H_4NO_2$: forms steel-blue needles, soluble only in excess of alkali.—$\{C_6H_4(NO_2).N_2.(C_6H_4NO_2)\}_2Cu$.—$\{C_6H_4(NO_2).N_2.(C_6H_4NO_2)\}_2Cd$.—$\{C_6H_4(NO_2).N_2.(C_6H_4NO_2)\}_2Co$.

***m*-Diazo-nitro-benzene-*p*-nitro-anilide** [3 or 4:1] $C_6H_4(NO_2).N_2.NH.C_6H_4(NO_2)$ [1:4 or 3]. [211°]. From diazotised *m*-nitro-aniline hydrochloride and *p*-nitro-aniline; or from diazotised *p*-nitro-aniline hydrochloride and *m*-nitro-aniline (Meldola a. Streatfeild, *C. J.* 51, 103, 439). Yellow needles (from alcohol). Dissolves in NaOHAq, forming a red solution. Cold aqueous HCl gives *m*- and *p*-diazo-nitro-benzene chlorides and *m*- and *p*-nitro-aniline.

***m*-Diazo-nitro-benzene-*m*-nitro-benzyl-anilide** [3:1] $C_6H_4(NO_2).N_2.NC_7H_7.C_6H_4(NO_2)$ [1:3]. [142°]. From *m*-diazo-nitro-benzene-*m*-nitro-anilide, alcoholic KOH, and benzyl chloride (M. a. S.). HClAq at 100° gives *m*-chloro-nitro-benzene and *m*-nitro-benzyl-aniline.

***p*-Diazo-nitro-benzene-*p*-nitro-benzyl-anilide** [4:1] $C_6H_4(NO_2).N_2.NC_7H_7.C_6H_4(NO_2)$ [1:4]. [190°]. From *p*-diazo-nitro-benzene-*p*-nitro-benzyl-anilide, alcoholic KOH, and C_7H_7Cl (Meldola a. Streatfeild, *C. J.* 51, 112). Minute yellow needles. Conc. HCl decomposes it at 100° into *p*-nitro-benzyl-aniline and *p*-chloro-nitro-benzene.

p-Diazo-nitro-benzene-m-nitro-benzyl-anilide [4:1] $C_6H_4(NO_2).N_2.C_7H_6.C_6H_4(NO_2)$ [1:3]. [180°]. From *m*-diazo-nitro-benzene-*p*-nitro-anilide alcoholic KOH, and benzyl chloride (Meldola a. Streatfeild, *C. J.* 51, 114).

***m*-Diazo-nitro-benzene-*m*-nitro-ethyl-anilide** [3:1] $C_6H_4(NO_2).N_2.NEt.C_6H_4(NO_2)$ [1:3]. [119°]. From *m*-diazo-nitro-benzene-*m*-nitro-anilide by treatment with KOH and EtI. Also from *m*-diazo-*p*-nitro-benzene and *m*-nitro-ethyl-aniline. Needles. Cold conc. HCl forms *m*-diazo-nitro-benzene chloride and *m*-nitro-ethyl-aniline (Meldola a. Streatfeild, *C. J.* 51, 108, 441).

***p*-Diazo-nitro-benzene-*p*-nitro-ethyl-anilide** [4:1] $C_6H_4(NO_2).N_2.NEt.C_6H_4(NO_2)$ [1:4]. [192°]. Formed by the action of EtI and KOH upon *p*-diazo-nitro-benzene-*p*-nitro-ethyl-anilide (Meldola a. Streatfeild, *C. J.* 49, 631). Or from diazotised *p*-nitro-aniline and *p*-nitro-ethyl-aniline (M. a. S., *C. J.* 51, 111, 442). Yellow needles, v. sl. sol. alcohol, insol. alkalis. Decomposed by cold HCl into *p*-diazo-nitro-benzene chloride and *p*-nitro-ethyl-aniline.

***p*-Diazo-nitro-benzene-*m*-nitro-ethyl-anilide** [4:1] $C_6H_4(NO_2).N_2.NEt.C_6H_4(NO_2)$ [1:3]. [187°]. From diazotised *p*-nitro-aniline and *m*-nitro-ethyl-aniline (Meldola a. Streatfeild, *C. J.* 51, 111, 442). Orange needles (from alcohol). V. sl. sol. alcohol. Cold conc. HCl gives *m*-nitro-ethyl-aniline and *p*-diazo-nitro-benzene chloride.

***m*-Diazo-nitro-benzene-*p*-nitro-ethyl-anilide** (?). [3:1] $C_6H_4(NO_2).N_2.Et.C_6H_4(NO_2)$ [1:4]. [148°]. Prepared by digesting the potassium salt of *m*-diazo-nitro-benzene-*p*-nitro-anilide dissolved in alcohol with EtI (Meldola a. Streatfeild, *C. J.* 51, 105). Small yellow needles. Heated with HCl at 100° it gives *m*- and *p*-nitro-ethyl-anilines and *m*- and *p*-chloro-nitro-benzenes. By cold HCl it is resolved into *m*- and *p*-diazo-nitro-benzene chlorides and *m*- and *p*-nitro-ethyl-anilines.

***m*-Diazo-nitro-benzene-*p*-nitro-ethyl-anilide** [3:1] $C_6H_4(NO_2).N_2.NEt.C_6H_4(NO_2)$ [1:4]. [175°]. From diazotised *m*-nitro aniline and *p*-nitro-ethyl-aniline (Meldola a. Streatfeild, *C. J.* 51, 110). Yellow needles (from alcohol). V. sl. sol. alcohol. With conc. HClAq it forms *p*-nitro-aniline and *m*-diazo-nitro-benzene chloride.

***p*-Diazo-nitro-benzene-piperidide** [4:1] $C_6H_4(NO_2).N_2.NC_5H_{10}$. [97°] (Wallach, *A.* 235, 264).

***m*-Diazo-nitro-benzene sulphonic acid**

$$C_6H_3\overset{(3)}{(NO_2)}\Big<\begin{array}{l}N_2\ (1)\\ \ |\\ SO_3\ (6)\end{array}$$

Formed by diazotisation of *m*-nitro-aniline sulphonic acid (1:3:6). White microscopic tables. By heating with absolute alcohol under an extra pressure of 400 mm. it is converted into *p*-nitro-benzene sulphonic acid (Limpricht, *B.* 18, 2186).

Diazo-nitro-benzene disulphonic acid

$C_6H_2(SO_3H)(NO_2)\Big<\begin{matrix}N_2\\SO_3\end{matrix}\Big>$. Formed by diazotising *m*-nitro-aniline disulphonic acid (Limpricht, *B.* 8, 289). Boiling alcohol forms *m*-nitro-benzene disulphonic acid.

Diazo-nitro-benzoic acid

$C_6H_3(NO_2)\Big<\begin{matrix}N_2\\CO_2\end{matrix}\Big>$. Explosive yellow laminæ (Salkowski, *A.* 173, 63).

[illegible] formed by diazotising nitro-amido-tetra-oxy-benzene (Nietzki a. Benkiser, *B.* 18, 501).—$C_6(NO_2)(N_2OH)(OH)(ONa)O_2aq$: long yellow explosive needles.—$C_6(NO_2)(N_2OH)(OH)(OAg)O_2$: yellow explosive plates.

Diazo-nitro-phenol $C_6H_3(NO_2)\Big<\begin{matrix}N_2\\O\end{matrix}\Big>$. From $C_6H_3(OH)(NH_2)(NO_2)$ [1:2:4] by diazotisation (Griess, *A.* 113, 212). Brownish-yellow granular mass; v. sl. sol. hot water, v. sol. alcohol. Explodes at 100°.

Methyl ether.
Nitrate $C_6H_3(NO_2)(OMe).N_2.NO_3$. Formed by diazotising nitro-anisidine (Griess, *J.* 1866, 459).
Platinochloride $\{C_6H_3(NO_2)(OMe)N_2Cl\}_2PtCl_4$.
Perbromide $C_6H_3(NO_2)(OMe).N_2Br_3$.
Imide $C_6H_3(NO_2)(OMe)N_3$: needles.
Methoxy-nitranilide
$C_6H_3(NO_2)(OMe).N_2.NH.C_6H_3(NO_2)(OMe)$. Formed by passing nitrous acid into an alcohol solution of nitro-anisidine (Griess, *A.* 121, 278).

Diazo-di-nitro-phenol $C_6H_2(NO_2)_2\Big<\begin{matrix}N_2\\O\end{matrix}\Big>$. Formed by passing nitrous acid into an alcoholic solution of di-nitro-amido-phenol (picramic acid (Griess, *A.* 113, 205). Yellow plates (from alcohol).

Diazo-nitro-β-phenyl-propionic acid [3:4:1] $C_6H_3(NO_2)(N_2.OH)C_2H_4.CO_2H$. *Nitro-diazo-hydrocinnamic acid.* The nitrate is formed by the action of ethyl nitrite and HNO_3 on (3:4:1)-nitro-amido-β-phenyl-propionic acid. It forms short colourless needles which explode feebly on heating. Heated with alcohol it gives *m*-nitro-hydrocinnamic acid (Gabriel, *B.* 15, 845).

Diazo-nitroso-methyl-nitro-benzene *v.* Diazo-nitro-benzaldoxim.

***p*-Diazo-nitroso-oxindole chloride**

$C_8H_5N_4O_2Cl$ or $C_6H_3(N{:}N.Cl)\Big<\begin{matrix}C(N.OH)\\NH\end{matrix}\Big>CO$.

p-Diazo-dioxindole-oxim chloride. Small yellow needles. Prepared by the action of amyl nitrite on a solution of amido-oxindole in HCl. Is only slightly attacked by boiling alcohol (Gabriel a. R. Meyer, *B.* 14, 832; *C. C.* 1885, 516).

***o*-Diazo-*p*-nitro-toluene-piperidide** $C_{12}H_{16}N_4O_2$ *i.e.* [1:4:2] $C_6H_3Me(NO_2).N_2.NC_5H_{10}$. [51°]. From *p*-nitro-*o*-toluidine [107°] by diazotisation of its hydrochloride and subsequent addition of piperidine (Wallach, *A.* 235, 248).

***o*-Diazo-nitro-toluene *p*-sulphonic acid**

$C_6H_2Me(NO_2)\Big<\begin{matrix}N_2\\SO_3\end{matrix}\Big>$. Formed by dissolving *o*-toluidine *p*-sulphonic acid in fuming HNO_3 and ppg. with ice-water (Hayduck, *A.* 172, 117). Boiling alcohol under 1160 mm. pressure does not attack it.

***p*-Diazo-nitro-toluene *o*-sulphonic acid.** Formed by dissolving *p*-toluidine *o*-sulphonic acid in cold fuming HNO_3 (Weckwarth, *A.* 172, 202). Large dark-red prisms. Alcohol heated with it under 1,000 mm. pressure gives nitro-toluene sulphonic acid (Pagel, *A.* 176, 304).

***p*-Diazo-nitro-toluene *m*-sulphonic acid** $C_6H_2Me(NO_2)N_2SO_3$ [1:2:4:5]. Formed by dissolving *p*-toluidine *m*-sulphonic acid in fuming HNO_3 (Pechmann, *A.* 173, 214), and also from $C_6H_2Me(NO_2)(NH_2)SO_3H$ [1:2:4:5] and nitrous

acid. Insol. cold water; on boiling with water only ⅔ of the theoretical quantity of nitrogen comes off; when boiled with Fe_2Cl_6 all comes off. Boiling alcohol does not affect it, but in a sealed tube at 100° it is converted into *o*-nitro-toluene *m*-sulphonic acid.

p-Diazo-di-nitro-toluene o-sulphonic acid

$C_6HMe(NO_2)_2<{N_2 \atop SO_3}>$. From *p*-toluidine *o*-sulphonic acid and fuming HNO_3 (Pagel, *A.* 176, 306). Yellowish needles. Not affected by alcohol boiling under 1,000 mm. pressure.

Diazo-oxy-acrylic ether (?)

$C_5H_6N_2O_3$ *i.e.* $CN_2:C(OH).CO_2Et$ (?). (142°) at 717 mm. V.D. = 5·0 (obs.). Yellow oil of strong peculiar odour. Volatile with steam.

Formation.—Gelatine, swollen with water, is warmed with absolute alcohol whilst HCl gas is passed in, it soon dissolves and after distilling off the alcohol a thick brown syrup is left; the latter, which appears to be the hydrochloride of amido-oxy-acrylic ether $CH(NH_2):C(OH).CO_2Et$ yields the diazo-ether when its concentrated aqueous solution is treated with $NaNO_2$; it is purified by distillation with steam; the yield is 150 grms. from 400 grms. of gelatine.

Reactions.—Acids eliminate its nitrogen, but it is very stable towards alkalis, with the exception of NH_3, which even in the cold soon splits off CO_2 and alcohol. By zinc-dust and acetic acid it is reduced first to a hydrazine and finally to an amido-acid. An ethereal solution of iodine converts it into di-iodo-oxy-acrylic ether $CI_2:C(OH).CO_2Et$ which on treatment with cold aqueous NH_3 loses CO_2 and alcohol and yields di-iodo-vinyl-amine $CI_2:CH(NH_2)$. It reduces $AgNO_3$ in the cold (Buchner a. Curtius, *B.* 19, 850).

Diazo-o-oxy-benzoic acid

$$C_6H_3(CO_2H)<{O \atop N_2} \quad [CO_2H:O:N = 1:6:3].$$

Diazo-salicylic acid. Formed by passing N_2O_3 into an aqueous or alcoholic solution of hydrochloride of amido-salicylic acid and concentrating. Crystallised from water (Schmitt, *J.* 1864, 384; Goldberg, *J. pr.* [2] 19, 362; P. F. Frankland, *C. J.* 37, 749). Slender needles.

Reactions.—1. Boiled with conc. HI it gives iodo-salicylic acid [196°] (*q. v.*). 2. *Mercaptan* at 170° gives salicylic acid (Schmitt a. Mittenzwey, *J. pr.* [2] 18, 193).

Chloride.—$C_6H_3(CO_2H)(OH)N_2Cl$.—Platino-chloride $\{C_6H_3(CO_2H)(OH)N_2Cl\}_2PtCl_4$.

Diazo-p-oxy-benzoic-amido-oxy-benzoic acid. *Dimethyl derivative.*

Diazo-amido-anisic acid

$C_6H_3(OMe)(CO_2H).N_2:NH.C_6H_3(OMe)(CO_2H)$. Formed by passing nitrous acid gas into a cold alcoholic solution of amido-anisic acid (Griess, *A.* 113, 337; 117, 45). Amorphous powder, insol. water, alcohol, and ether. Warm conc. HCl converts it into a red acid $C_{16}H_{14}O_7$.—$Na_2A''1\frac{1}{2}aq.$—$K_2A''2aq.$—Et_2A'': narrow leaflets.

Diazo-oxy-cinnamic acid. *Methyl derivative* $C_6H_3(N_2OH)(OMe).CH:CH.CO_2H$ [5:2:1]. Formed by diazotising methoxy-amido-cinnamic acid. The chloride forms yellow crystals, which decompose at about 102°. The nitrate $C_6H_3(N:N.NO_3)(OMe)(C_2H_2.CO_2H)$ crystallises in yellow needles, which explode at 152°, nearly insoluble in cold water, alcohol, and ether (Schnell, *B.* 17, 1385).

o-diazo-phenol. *Chloride* $C_6H_4(OH)N_2Cl$. By passing N_2O_3 into an alcoholic solution of the hydrochloride of *o*-amido-phenol, and then adding ether (Schmitt, *B.* 1, 67; Böhmer, *J. pr.* 132, 460). Rhombohedra. Bromine-water added to its aqueous solution forms a yellow pp. of diazo-dibromo-phenol (*q. v.*).

Sulphite $C_6H_4(OH).N_2.SO_3K$ aq. Golden scales, got by adding $KHSO_3$ to $C_6H_4(OH).N_2Cl$ (Schmitz a. Glutz, *B.* 2, 51; Reisenegger, *A.* 221, 314).

Platinochloride $(C_6H_4(OH)N_2Cl)_2PtCl_4$.

m-Diazo-phenol. *Ethyl derivative* (Wagner, *J. pr.* [2] 32, 70).

p-Diazo-phenol. *Nitrate* $C_6H_4(OH).N_2NO_3$. Formed by passing nitrous acid gas into a cold ethereal solution of phenol (Weselsky, *Sitz. B.* 1875, 9; *B.* 8, 895), or of *p*-nitroso-phenol (Jäger, *B.* 8, 894).

Preparation.—By passing N_2O_3 into alcoholic solution of hydrochloride of *p*-amido-phenol, adding strong HNO_3 and cooling strongly (Böhmer, *J. pr.* 132, 450).

Reactions.—1. By warming with dilute HBr (15 per cent. solution) it does not give off nitrogen, as diazo-benzene nitrate would do, but forms di-azo-di-bromo-benzene in accordance with the equation:

$$6C_6H_4<{OH \atop N_2NO_3} + 9HBr =$$

$$3C_6H_2Br_2<{O \atop N_2} + 3C_6H_4<{OH \atop N_2Br} + 3NO_2 + 3NO + 9H_2O.$$

Chloride $C_6H_4(OH).N_2Cl$. Formed by diazotising *p*-amido-phenol hydrochloride. Converted into hydroquinone by boiling conc. HCl or dilute H_2SO_4 (Schuler, *B.* 9, 1160). Heated with mercaptan it gives phenol and $(C_2H_5)_2S_2$ (Schmitt a. Mittenzwey, *J. pr.* [2] 18, 194).—$(C_6H_4(OH).N_2Cl)_2PtCl_4$.

Bromide $C_6H_4(OH)N_2Br$. Formed by passing N_2O_3 into an alcoholic solution of the hydrobromide of *p*-amido-phenol (C. Böhmer, *J. pr.* 132, 451). Precipitated by ether.

Platinobromide $(C_6H_4(OH)N_2Br)_2PtBr_4$. Needles grouped in spherical segments. Got by adding an aqueous solution of $PtBr_4$ (prepared like $PtCl_4$ by dissolving *spongy* platinum in HBr mixed with HNO_3 and evaporating) to one of diazo-phenol hydrobromide. If left for several days in contact with their mother liquor, the crystals absorb eight molecules of water of crystallisation changing to blood-red twin crystals resembling gypsum. These are insoluble in ether, CS_2 and $CHCl_3$, difficultly soluble in water. The salt heated with 10 pts. of Na_2CO_3 does not yield bromophenol.

Sulphate $C_6H_4(OH)N_2.SO_4H$. Obtained by adding dilute H_2SO_4 to an alcoholic solution of the hydrochloride of *p*-amido-phenol, passing in N_2O_3 and adding ether. Needles. Does not explode when heated. Converted by boiling HBr into the bromo-phenyl ether of hydroquinone (*q. v.*).

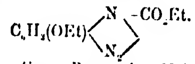
Sulphite $HO.C_6H_4.N_2.SO_3K$. From *p*-amido-phenol, HCl, $NaNO_2$, and K_2SO_3 (Reisenegger, *A.* 221, 316). Yellowish plates.

Ethyl derivative $C_6H_4(OEt)N_2OH$. Salts.—$C_6H_4(OEt)N_2Cl$. From *p*-amido-phenetol hydrochloride by solution in alcohol and treatment with N_2O_3. Precipitated by ether as an oil.

Crystallises when cooled to −18°. But if H_2SO_4 be added to the alcoholic solution of the chloride, avoiding rise of temperature, crystals of the sulphate $C_6H_4(OEt)N_2.SO_4H$ separate. Boiled with water this forms $C_6H_4(OEt)(OH)$, hydroquinone mono ethylic ether (*q. v.*) (Hantzsch, *J. pr.* 130, 461).

Methyl derivative. The salts are formed by diazotising *p*-anisidine (Salkowski, *B.* 7, 1009): $C_6H_4(OMe).N_2NO_3$. - $C_6H_4(OMe).N_2.SO_4H$.

Diazo-phenol-carbamic ether. *Ethyl derivative*



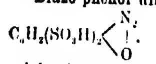
Preparation.—By passing N_2O_3 into a solution of the hydrochloride of ethoxy-amido-phenyl-urethane, $C_6H_3(OEt)(NH_2).NH.CO_2Et$, HCl (Kohler, *J. pr.* [2] 29, 273).

Properties.—Slender, silvery-white matted needles. Insol. water, sol. alcohol, ether, and glacial acetic acid. Decomposes below 100°.

Reactions. 1. Does not explode.—2. Not affected by boiling alcohol.—3. Boiled with soda, it is decomposed with evolution of nitrogen.

Diazo-phenol sulphonic acids $C_6H_3(N_2OH)(OH)(SO_3H)$ [1:4:3] and [3:4:1] are unstable crystalline acids obtained by diazotising the corresponding amido-phenol sulphonic acids (Bennewitz, *J. pr.* [2] 8, 52).

Diazo phenol disulphonic acid



From *p*-amido-phenol disulphonic acid (*q. v.*) (Wilsing, *A.* 215, 238).

Salt. K_2A''aq. Small sulphur-yellow needles. Warmed with water it forms hydroquinone disulphonic acid.

p-p-**Tetra-azo-diphenyl**

Nitrate $NO_3.N_2.C_6H_4.C_6H_4.N_2NO_3$. Formed by passing nitrous acid gas into an alcoholic solution of nitrate of benzidine, and ppg. with ether (Griess, *Tr.* 1864, iii. 719). White needles, v. sol. water, m. sol. alcohol, insol. ether. Explodes when heated. Boiling water forms *p-p*-di-oxy-diphenyl.

Perbromide $Br_3N_2.C_6H_4.C_6H_4.N_2Br_3$.

Imide $N_3.C_6H_4.C_6H_4.N_3$. [127°]. White plates.

Platinochloride $(ClN_2.C_6H_4.C_6H_4.N_2Cl)PtCl_4$: yellow plates.

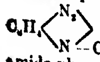
Sulphate $(HSO_4N_2.C_6H_4.C_6H_4.N_2SO_4H)H_2SO_4$: white needles.

Anilide $PhNH.N_2.C_6H_4.C_6H_4.N_2.NHPh$: large-shaped crystals, insol. water. Explosive.

Piperidide $C_5H_{10}N.N_2.C_6H_4.C_6H_4.N_2.NC_5H_{10}$. From benzidine by diazotisation and treatment with piperidine. Insol. water, sl. sol. alcohol, v. sol. ether (Wallach. *A.* 235, 271).

m-m-**Tetra-azo-diphenyl** (Brunner a. Witt, *B.* 20, 1028).

Diazo-phenyl-carbamic ether



$-CO_2Et$. Formed by diazotising *o*-amido-phenyl-carbamic ether (Rudolph, *B.* 12, 1296).

Hexa-azo-tri-phenyl-carbinol

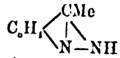
Chloride $\{C_6H_4(N_2Cl)\}_3COH$. *Diazo-p-rosaniline chloride.* Formed by diazotising *p*-rosaniline hydrochloride (E. a. O. Fischer, *A.* 194, 274).—$C_{19}H_{13}N_6Cl_3 3AuCl_3$.

Hexa-azo-tri-phenyl-carbinyl cyanide

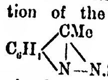
Chloride $\{C_6H_4(N_2Cl)\}_3C.CN$ 2aq. From hydrocyano-*p*-rosaniline hydrochloride by diazotisation. Slender needles, v. sol. water. Gives, with boiling water, $(C_6H_4OH)_3C.CN$ (Fischer, *A.* 194, 275).

Hexa-azo-tri-phenyl-methane chloride $(C_6H_4N_2Cl)_3CH$. *Diazo-p-leucaniline.* Formed by diazotising tri-amido-tri-phenyl-methane-hydrochloride (E. a. O. Fischer, *A.* 194, 269). Gives *p*-rosolic acid (aurin) when boiled with water.

Di-azo-phenyl methyl ketone sulphite of sodium $CH_3.CO.C_6H_4.N_2.SO_3K$. Formed by diazotising *o*-amido-acetophenone and treating the product with K_2SO_3. On reduction it gives the hydrazine salt: $CH_3.CO.C_6H_4.NH.NHSO_3K$ whence HCl forms methyl-indazol,



(*v.* Indazol). The aqueous solution of the hydrazine salt changes to



methyl-indazol sulphonate of sodium (Fischer a. Tafel, *A.* 227, 305).

Hexa-azo-di-phenyl-tolyl-carbinol.

Chloride $(C_6H_4N_2Cl)_2C(OH).C_6H_3MeN_2Cl$. *Diazo-rosaniline.* Formed by diazotising rosaniline hydrochloride (Caro a. Wanklyn, *Z.* 1866, 511; E. a. O. Fischer, *A.* 194, 279). Gives rise to rosolic acid when boiled with water.—$(C_{20}H_{15}N_6Cl_3)_2 3PtCl_4$ 6aq.—$C_{20}H_{15}N_6Cl_3 3AuCl_3$.

Hexa-azo-di-phenyl-tolyl-carbinyl cyanide.

Chloride $(C_6H_4N_2Cl)_2:C(CN).C_6H_3MeN_2Cl$. *Diazohydrocyan-rosaniline.*—*Gold salt.*—$C_{20}H_{14}(CN)N_6Cl_3 3AuCl_3$.

Diazo-resorcin chloride. *Diethyl ether* $C_6H_3(OEt)_2N_2Cl$. From the amido- compound (Pukall, *B.* 20, 1136). Unstable crystals.

Diazo-rosaniline (*v. supra*).

Diazo-salicylic acid *v.* Diazo-oxy-benzoic acid.

Diazo-succinamic acid

$CO_2H.CH_2.CN_2.CONH_2$.

Methyl ether A'Me: [84°]; long yellow prisms (from alcohol). Formed by the action of aqueous NH_3 upon methyl diazo-succinate. By decomposition with cold slightly acidified water it yields methyl fumaramate and methyl malamate. Heated with benzoic acid at 140°–150° it gives methyl benzoyl-malamate. Iodine in ethereal solution converts it into methyl di-iodo-succinamate—$CO_2Me.CH_2.CI_2.CONH_2$ (Curtius a. Koch, *B.* 19, 2460).

Ethyl ether $C_2H_2N_2(CONH_2)(CO_2Et)$.—[112°]; long thin yellow prisms; easily soluble in hot water and alcohol, sparingly in cold water and ether. It is not altered by boiling with pure water, but by acids and alkalis is at once decomposed with evolution of nitrogen. Reduced to aspartic ether by zinc-dust and acetic acid (Curtius a. Koch, *B.* 18, 1293).

Diazo-succinic acid $C_2H_2N_2(CO_2H)_2$. The di-methyl and di-ethyl ethers of this acid are obtained by mixing iced solutions of the hydrochlorides of the aspartic ethers $CO_2R.CH(NH_3Cl).CH_2.CO_2R$ and sodium nitrite, and adding a few drops of dilute H_2SO_4, after

which the product is shaken out with ether. The ethers form dark-yellow oils which have not yet been obtained in a pure state. By boiling with water or aqueous acids they are decomposed with evolution of nitrogen and formation of the corresponding fumaric ether. They decompose spontaneously on keeping, evolving nitrogen and forming azinsuccinic ethers $(CO_2R)_2C_2H_2:N.N:C_2H_2(CO_2R)_2$. Strong aqueous NH_3 converts them into diazo-succinamic ethers.

***p*-Diazo-toluene.**

Salts.—The preparation and properties of these salts resemble those of the corresponding diazo-benzene salts (Griess, *C. J.* 20, 86).—$C_6H_4Me.N_2.NO_3$: long slender white needles.—$(C_6H_4Me.N_2Cl)_2PtCl_4$: yellow prismatic crystals. $C_6H_4Me.N_2SO_4H$.—$C_6H_4Me.N_2Br_3$.

Dicyanide $C_9H_8N_4$ or $C_6H_4Me.N_2.CN,HCN$. [78°]. Needles or leaflets. Formed by the action of a diazo-toluene salt on a solution of KCN (*B.* 12, 1638).

Anilide $C_6H_4Me.N_2.NHPh$ or, alternatively, $Ph.N_2.NH.C_6H_4Me$. From *p*-toluidine and diazobenzene nitrate or from aniline and *p*-diazotoluene nitrate (Griess, *A.* 137, 60; *B.* 7, 1619). Narrow yellow leaflets. By warming with phenol it gives a mixture of aniline, *p*-toluidine, benzene-azo-phenol and *p*-toluene-azo-phenol; similarly with resorcin (Heumann a. Oeconomides, *B.* 20, 907).

p-Chloro-anilide. Formed from *p*-chloro-diazo-benzene and *p*-toluidine. By heating with phenol it gives *p*-toluene-azo-phenol and *p*-chloraniline (Heumann a. Oeconomides, *B.* 20, 909).

Piperidide $C_{12}H_{17}N_3$ *i.e.* $C_7H_7.N_2.NC_5H_{10}$ [41°]. From $CH_3.C_6H_4.N_2Cl$ and piperidine. Prisms (from alcohol or ether). Insol. water. Dry HCl passed into its solution in petroleum-ether appears to form an unstable hydrochloride, quickly decomposing into diazotoluene chloride and piperidine hydrochloride (Wallach, *A.* 235, 244).

p-Toluide $C_6H_4Me.N_2.NH.C_6H_4Me$. [116°]. Formed by passing nitrous acid gas into a solution of *p*-toluidine in alcohol and ether (Griess, *A.* 121, 277; when pure (by digestion with alcoholic $(NH_4)_2S$) it forms nearly colourless large thin prisms (Bernthsen a. Goske, *B.* 20, 928).

p-Ethyl-toluide $C_6H_4Me.N_2.NEt.C_6H_4Me$. Decomposed by acids into ethyl-*p*-toluidine and *p*-diazo-toluene chloride (Gastiger, *Bl.* [2] 42, 342).

***o*-Diazo-toluene-*o*-toluide**

[2:1] $C_6H_4Me.N_2.NH.C_6H_4Me$ [1:2]. [51°]. Orange-yellow powder of microscopic needles. Prepared by adding sodium nitrite (1 mol.) to an aqueous solution of *o*-toluidine (2 mols.) and HCl (3 mols.) and then neutralising the HCl with sodium acetate, the temperature being kept below −5° during the whole reaction. It is crystallised by dissolving in cold alcohol and adding ice (Fischer a. Wimmer, *B.* 20, 1582).

***o*-Diazo-toluene-azo-toluene** $C_{14}H_{13}N_4.OH$ *i.e.*

$$C_7H_6\left\langle\begin{array}{l}N-N.OH\\ |\qquad |\\ N-N.C_7H_7\end{array}\right.$$

. (?) Obtained by diazotising toluene-azo-*o*-toluidine; the salts crystallise out when a stream of nitrous acid gas is passed into an alcoholic solution of toluene-*o*-azo-toluidine and an excess of acid, or upon subsequent addition of a little ether. On heating with water or alcohol it decomposes, evolving nitrogen like ordinary diazo-compounds. By $SnCl_2$ or SO_2 it is not reduced to a hydrazine but gives a stable compound $C_{14}H_{14}N_4$ which probably has the constitution

$$C_7H_6\left\langle\begin{array}{l}N-NH\\ |\qquad |\\ N-NC_7H_7\end{array}\right.,$$

by bromine this body is reconverted into the diazo-perbromide. By zinc-dust and alcohol it is converted into *m*-toluene-*p*-azo-toluene [58°] with evolution of nitrogen. The diazo-imide loses nitrogen on heating and yields tolyl-azimido-toluene

$$C_7H_6\left\langle\begin{array}{c}N\\ |\\ N\end{array}\right\rangle N.C_7H_7$$

identical with that obtained by oxidation of toluene-azo-*o*-toluidine. *o*-Diazo-toluene-azo-toluene reacts with amines and phenols like an ordinary diazo-compound; the products, however, reduce to a diamine or amido-phenol and tolyl-azimido-toluene. All the salts have a deep orange-yellow colour and are tolerably stable.—$C_{14}H_{13}N_4.Cl$*: red granular crystals.—$(C_{14}H_{13}N_4Cl)_2PtCl_4$: yellow acicular crystals.—$C_{14}H_{13}N_4.NO_3$*: slender red pointed crystals.—$C_{14}H_{13}N_4.SO_4H$*: red interwoven needles.—$C_{14}H_{13}N_4.Br_3$: [125°], long glistening red needles or compact crystals.

Imide $C_{14}H_{13}N_3$: [85°], thick yellowish red crystals; formed by the action of alcoholic NH_3 upon the perbromide (Zincke a. Lawson, *B.* 19, 1452).

Product of Reduction $C_{14}H_{14}N_4$ probably

$$C_7H_6\left\langle\begin{array}{l}N-NH\\ |\qquad |\\ N-N.C_7H_7\end{array}\right.$$

[168°]. Long colourless needles. V. sol. hot alcohol, sl. sol. ether and chloroform, insol. water. It has no basic properties. It is not affected by reducing agents. Bromine in alcoholic or acetic acid solution readily converts it into *o*-diazo-toluene-azo-toluene perbromide. On addition of Ag_2O to its alcoholic solution nitrogen is evolved and *m-p*-azotoluene [58°] is formed.

Acetyl derivative $C_{14}H_{13}N_4Ac$ [134°]: glistening white plates (Zincke a. Lawson, *B.* 19, 1457).

***p*-Diazo-toluene-azo-toluene**

[2:1] $C_6H_4(CH_3)-N_2-C_6H_3(CH_3).N_2OH$ [1:3:4]. Prepared by dissolving toluene-azo-*p*-toluidine in alcohol, adding an excess of HCl, diazotising by passing N_2O_3 into the well-cooled solution, and precipitating the diazo-salt with ether. By reduction with $SnCl_2$ or zinc-dust and acetic acid in cold dilute aqueous solution it is split up (without formation of a hydrazine) into *o*-toluidine and tolylene-*p*-diamine.

Salts.—*$C_{14}H_{13}N_4.NO_3$: slender brownish-yellow needles, m. sol. water and alcohol.—$C_{14}H_{13}N_4.Br_3$: yellow crystalline pp. which changes on standing to small violet needles.—$C_{14}H_{13}N_4.SO_3Na$: glistening scales (from alcohol), v. sol. hot. alcohol, sl. sol. water.

Imide $C_{14}H_{13}N_5$: [60°]; long plates; sol. alcohol and acetic acid (Zincke a. Lawson, *B.* 20, 1181).

***o*-Diazo-toluene *m*-sulphonic acid**

$$^{*}MeC_6H_3\left\langle\begin{array}{c}N{:}N\\ SO_3\end{array}\right\rangle\left[\begin{array}{cc}1 & 2\\ & 5\end{array}\right].$$

Precipitated as a white powder when nitrous gas is passed into a

cold solution of *o*-toluidine sulphonic acid. Explodes feebly at 100° (Nevile a. Winther, *C. J.* 37, 628).

o-Diazo-toluene p-sulphonic acid. Minute monoclinic prisms (Hayduck, *A.* 172, 213; 174, 344). Boiling alcohol produces $Me.C_6H_3(OEt).SO_3H$ [1:2:4].

p-Diazo-toluene o-sulphonic acid. Yellow or brown needles (Ascher, *A.* 161, 8; Jensen, *A.* 172, 235). Heated with alcohol under pressure it gives $MeC_6H_3(OEt)(SO_3H)$ Remsen a. Palmer, *Am.* 8, 243).

p-Diazo-toluene m-sulphonic acid $MeC_6H_3<{N:N \atop SO_3}>$ $\left[1{4 \atop 3}\right]$. More soluble than the corresponding *o*-compound (Nevile a. Winther, *C. J.* 37, 631). Prepared by passing nitrous acid gas into *p*-toluidine sulphonic acid suspended in alcohol. Hot alcohol gives toluene *m*-sulphonic acid (Petermann, *A.* 173, 201).

p-Diazo-toluene exo-sulphonic acid $C_6H_4<{N_2 \atop CH_2}>SO_2$. Heated with alcohol under 1,100 mm. pressure it gives $C_6H_4(OEt).CH_2.SO_3H$ (Mohr, *A.* 221, 219).

p-Diazo-toluene-sulphonic-amido-toluene sulphonic acid. *Amide* [1:4:2] $C_6H_3Me(SO_2NH_2)N_2.NH.C_6H_3Me.SO_2NH_2$ [2:1:4]. From $C_6H_3Me(NH_2)SO_2NH_2$ [1:2:4], alcohol, and nitrous acid gas (Paysan, *A.* 221, 211). Decomposed by HCl into N_2, $C_6H_3ClMe.SO_2NH_2$, and $C_6H_3(NH_2)Me.SO_2NH_2$.

o-Diazo-toluene disulphonic acid $C_6H_2Me(SO_3H)<{N_2 \atop SO_3}$ $\left[1{:}6{:}{2 \atop 3}\right]$. From N_2O_3 and aqueous *o*-toluidine disulphonic acid at 0° (Limpricht, *B.* 18, 2176; Hasse, *A.* 230, 291). Microscopic needles. Explosive. Heated with alcohol under pressure it gives $C_6H_2Me(OEt)(SO_3H)_2$. With HI it forms $C_6H_2MeI(SO_3H)_2$.

Salts.—KA'.—BaA'_2 4aq.—PbA'_2.

p-Diazo-toluene di-sulphonic acid $C_6H_2Me(SO_3H)<{N_2 \atop SO_3}$. Formed by diazotisation of *p*-toluidine-di-sulphonic acid. Yellowish crystals. By heating with HI it yields *p*-iodo-toluene-di-sulphonic acid; with HBr it yields *p*-bromo-toluene-di-sulphonic acid.

Salts.—$A'K$: large yellow prisms.—A'_2Ba: yellowish white needles.—A'_2Pb: small red prisms (Limpricht, *B.* 18, 2178).

[illegible]-Diazo-toluic-amido-toluic acid $C_6H_3Me(CO_2H).N_2.NH.C_6H_3Me.CO_2H$. From amido-toluic acid and nitrous ether (Griess, *A.* 117, 59). Minute yellow prisms (containing ½ aq); insol. water, alcohol, and ether.

o-Diazo-p-toluidine bromide. *Acetyl derivative* $C_6H_3Me(NHAc).N_2Br$ [1:4:2]. From $C_6H_3Me(NHAc)(NH_2)$ [1:4:2], conc. HBr and conc. $NaNO_2$ at 0° (Wallach, *A.* 235, 249).

Reactions.—1. Hot Ac_2O converts it into $C_6H_3Me(NHAc)(OAc)$ [132·5°].—2. Nitro-ethane and NaOEt give $C_6H_3Me(NHAc).N_2.CHMe(NO_2)$ [149°].—3. $HNEt_2$ gives $C_6H_3Me(NHAc)N_2.NEt_2$ [108°].—4. *Piperidine* gives the piperidide: $C_6H_3Me(NHAc).N_2.NC_5H_{10}$ [154°]. HCl passed into an alcoholic solution of this base gives a pp. of $C_6H_3Me(NHAc)N_2Cl$, [illegible] gives $C_6H_3Me(NHAc)Cl$.

Diazo-m-xylene-sulphonic acid $C_6H_2Me_2<{N_2 \atop SO_3}>$ [1:3:4:6]. White pp. Sparingly soluble in water. Decomposes at 60°-70°. Combines with phenols and amines. Formed by diazotisation of *m*-xylidine-sulphonic acid (Nölting a. Kohn, *B.* 19, 138).

Diazo-p-xylene-sulphonic acid $C_6H_2Me_2<{N_2 \atop SO_3}>$ $\left[1{:}4{2 \atop 5}\right]$. Yellowish white plates. Stable at ordinary temperature, decomposes on heating with water at 60°-70°. Formed by the diazotisation of *p*-xylidine-sulphonic acid $C_6H_2Me_2(NH_2)(SO_3H)$ [1:4:2:5] (Nölting a. Kohn, *B.* 19, 141).

DISAZO- COMPOUNDS. *Secondary azo-compounds.* Compounds containing two azo- groups of the form $C-N_2-C$. The general methods by which they may be prepared are given in the article on azo- colouring matters (p. 368). The nomenclature here used is like that used for azo- compounds. To find the name of a disazo-compound, write down the formula, strike out everything between the two N_2 groups, remove one of the N_2 groups, and join the remaining parts of the formula together and name the resulting azo- compound as directed on p. 369. Then insert after the word 'azo' the name of the central hydrocarbon, preceded by prefixes representing its substituents and followed by 'azo.'

Di-amido-benzene-azo-benzene-azo-benzene sulphonic acid [4:1] $C_6H_4(SO_3H)-N_2-C_6H_4-N_2-C_6H_3(NH_2)_2$ [1:2:4]. Formed by the combination of diazo-benzene-azo-benzene-*p*-sulphonic acid with *m*-phenylene diamine. Red microscopic needles. V. sl. sol. alcohol and ether. In H_2SO_4 it dissolves with a violet-blue colour.—KA'2aq: red glistening plates, sl. sol. hot, v. sl. sol. cold, water, dyes silk, wool, and cotton a brownish-red (Griess, *B.* 16, 2035).

Amido-sulpho-naphthalene-azo-diphenyl-azo-naphthylamine sulphonic acid

$$\begin{array}{l} [1{:}4{:}2]\ C_{10}H_5(NH_2)(SO_3H)-N_2-C_6H_4 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ [1{:}4{:}2]\ C_{10}H_5(NH_2)(SO_3H)-N_2-C_6H_4. \end{array}$$

Formed by combining diazotised benzidine with (α)-naphthylamine *p*-sulphonic acid. Dyes cotton from an alkaline bath scarlet, turned blue by a trace of acid. The aqueous solution is readily reduced by NH_3 and zinc-dust, giving benzidine and naphthylene-*o*-di-amine sulphonic acid (Witt, *B.* 19, 1719).

Benzene-azo-m-diamido-benzene-azo-benzene $C_6H_5-N_2-C_6H_2(NH)_2-N_2-C_6H_5$. [250°]. Formed by the combination of diazobenzene with chrysoïdine. Dark red needles or six-sided plates. Sol. hot chloroform and benzene, v. sl. sol. alcohol and ether, insol. water. Weak base. Salts.—$B'HCl$: violet-brown amorphous solid.—$B'_2H_2Cl_2PtCl_4$: violet-brown amorphous pp. (Griess, *B.* 16, 2028).

Benzene-azo-m-diamido-benzene-azo-benzene p-sulphonic acid $C_6H_4(SO_3H)-N_2-C_6H_2(NH_2)_2-N_2-C_6H_5$. Formed by the action of *p*-diazo-benzene-sulphonic acid on chrysoïdine. Dark-brown microscopic crystals. V. sl. sol. alcohol [illegible]

ether. AK: reddish-brown plates, sol. hot, sl. sol. cold, water (Griess, *B.* 16, 2032).

Benzene-azo-di-amido-benzene-azo-benzoic acid $C_6H_4(CO_2H)-N_2-C_6H_2(NH_2)_2-N_2-C_6H_5$. Formed by combining *m*-diazo-benzoic acid with chrysoïdine (Griess, *B.* 16, 2032). Brownish-red powder. Insoluble or nearly insoluble in all ordinary solvents. Soluble in alkalis with a brownish-red colour.

(a)-Benzene-azo-*m*-di-amido-benzene-azo-toluene $C_6H_5-N_2-C_6H_2(NH_2)_2-N_2-C_7H_7$. [192°]. Formed together with a small quantity of the (β)-isomeride by the combination of *p*-diazo-benzene with *p*-toluene-azo-phenylene-diamine. Dark-red glistening needles. Sol. ether, chloroform and hot benzene, insol. water and alcohol.

(β)-Benzene-azo-*m*-di-amido-benzene-azo-toluene $C_6H_5-N_2-C_6H_2(NH_2)_2-N_2-C_7H_7$. [225°]. Slender yellow needles. Sol. alcohol and ether, v. sl. sol. chloroform, sol. in water (Griess, *B.* 16, 2029).

Benzene-azo-*m*-di-amido-benzene-*p*-azo-toluene $C_7H_7-N_2-C_6H_2(NH_2)_2-N_2-C_6H_5$. [214°]. Formed by the combination of *p*-diazo-toluene with chrysoïdine (Griess, *B.* 16, 2030). Dark-red glistening needles. Sl. sol. chloroform, ether, and benzene.

Benzene-azo-benzene-azo-*p*-cresol
$C_6H_5-N_2-C_6H_4^{(4)}\ ^{(1)}-N_2-C_6H_3^{(5)}(CH_3)^{(2)}(OH)$. [160°]. Obtained by the action of diazo-benzene-azo-benzene chloride (by diazotising benzene-azo-aniline) on an alkaline solution of *p*-cresol (Nölting a. Kohn, *B.* 17, 354). Small brown needles. Sl. sol. alcohol, m. sol. chloroform, benzene, and acetic acid. Dissolves in H_2SO_4 with a reddish violet colour.

Benzene-azo-benzene-azo-ethyl-(β)-naphthyl-amine $C_6H_5-N_2-C_6H_4-N_2-C_{10}H_6.NHEt$. [142°]. Small red needles. Formed by heating ethyl-(β)-naphthyl-nitrosamine with an acetic acid solution of benzene-azo-aniline (Henriques, *B.* 17, 2670).

Benzene-azo-benzene-azo-(β)-naphthol
$C_6H_5-N_2-C_6H_4-N_2-C_{10}H_6.OH$. From diazotised benzene-azo-aniline and (β)-naphthol (Nietzki, *B.* 13, 1838). Brick-red powder.

Benzene-azo-benzene-azo-resorcin
$C_6H_5-N_2-C_6H_4-N_2-C_6H_3(OH)_2$. By the action of diazotised benzene-azo-aniline on resorcinol two isomerides are formed which are separated by their different solubilities in aqueous alkalis.

(a)-*Compound* [181°]. Brownish red powder consisting of microscopic tables. Dissolves with a carmine red colour in aqueous NaOH and in H_2SO_4. Sol. alcohol, ether, and chloroform.

(β)-*Compound* [215°]. Brown powder. Dissolves in alcoholic NaOH with a violet-blue colour and in H_2SO_4 with a pure blue colour, v. sl. sol. alcohol, ether, and chloroform, insol. aqueous NaOH (Wallach, *B.* 15, 2817).

Benzene-azo-methyl-pyrrol-azo-benzene
$C_6H_5-N_2-C_4H_2NMe-N_2-C_6H_5$

probably
$$\begin{array}{l} C_6H_5.N_2.C{=}CH \\ \quad\ \ |\quad\ \ NMe| \\ C_6H_5N_2.C{=}CH \end{array}$$
[196°]. Formed by the methylation of benzene-azo-pyrrol-benzene. Red plates (O. Fischer a. Hepp, *B.* 19, 2253).

Benzene-azo-oxy-benzene-azo-benzene
$C_6H_5-N_2^{(1)}-C_6H_3^{(4)}(OH)-N_2^{(2)}-C_6H_5$. *Benzene-disazo-phenol. Phenol-bi-diazo-benzene.* [131°]. Formed, together with benzene-azo-phenol, by treating diazo-benzene nitrate with $BaCO_3$ in the cold, or by the action of diazo-benzene nitrate upon a solution of benzene-azo-phenol in KOHAq (Griess, *A.* 137, 86; *B.* 9, 628). Brown lustrous needles or plates (from alcohol). V. sl. sol. water, v. sol. KOHAq, v. sl. sol. NH_3Aq, insol. Na_2CO_3Aq.

Methyl ether $C_{18}H_{13}N_4(OMe)$ [110°], small yellow crystals, v. sol. ether, benzene, acetone, and hot alcohol.

Acetyl derivative $C_{18}H_{13}N_4(OAc)$ [116°], small yellow needles, sol. alcohol, ether, and benzene.

Benzoyl derivative $C_{18}H_{13}N_4(OBz)$ [139°], small yellow needles, sl. sol. cold alcohol (Nölting a. Kohn, *B.* 17, 368).

Benzene-azo-di-oxy-benzene-azo-benzene
$C_6H_5-N_2-C_6H_2(OH)_2-N_2-C_6H_5$. By the action of diazo-benzene chloride on an alkaline solution of benzene-azo-resorcin two isomerides are formed which are separated by their solubility in aqueous alkalis. A third isomeride (γ)-is formed, together with benzene-azo-resorcin, by the action of diazo-benzene chloride on resorcin treated with KOH (1 mol.) in dilute aqueous solution.

(a) *Compound* [215°]. Brown felted needles. Dissolves easily with a red colour in aqueous NaOH and in H_2SO_4. Sl. sol. alcohol and ether, m. sol. chloroform. Its di-acetyl derivative forms brown glistening needles, [184°] (Wallach).

(β)-*Compound* [220°]. Microscopic needles. Sl. sol. alcohol and chloroform, insol. aqueous NaOH. Dissolves in H_2SO_4 with an indigo-blue colour, and in alcoholic NaOH with a red colour (Wallach, *B.* 15, 2816).

(γ)-*Compound* [222°]. Large red needles Sol. chloroform, v. sl. sol. alcohol. It dissolves in strong alkalis with a brownish-yellow colour; in H_2SO_4 with the same colour. By tin and HCl it is reduced to aniline and di-amido-resorcin.

Di-acetyl-derivative
$C_{18}H_{12}N_4(OAc)_2$ [138°], orange needles (Liebermann a. Kostanecki, *B.* 17, 880).

Benzene-azo-trioxy-benzene-azo-benzene
$C_6H_5-N_2-C_6H(OH)_3-N_2-C_6H_5$. *Phloroglucin-bi-diazo-benzene.* Yellowish-brown leaflets. Prepared by the action of diazobenzene nitrate on phloroglucin (Weselsky a. Benedikt, *B.* 12, 226).

Benzene-azo-dioxy-benzene-azo-naphthalene
$C_6H_5-N_2-C_6H_2(OH)_2-N_2-C_{10}H_7$. [155°]. From diazo-benzene chloride and an alkaline solution of *m*-di-oxy-benzene-azo naphthalene (Wallach, *B.* 15, 22).

Benzene-azo-di-oxy-benzene-azo-toluene
$C_6H_5-N_2-C_6H_2(OH)_2-N_2-C_6H_4(CH_3)$ [1:4]. Prepared by the action of diazo-benzene chloride on an alkaline solution of *m*-dioxy-benzene-azo-toluene, or of diazo-toluene chloride on an alkaline solution of benzene-azo-resorcin; in either case the same three isomerides are simultaneously produced and are separated by means of their different solubilities.

(a)-*Compound* [196°]. Golden brown needles. Dissolves with a red colour in H_2SO_4 and NaOH.

Sol. alcohol and chloroform. Its di-acetyl-derivative forms yellow needles, [176°].

(a')-*Compound* [241°]. Dissolves with a red colour in H_2SO_4 and in aqueous NaOH. Its di-acetyl-derivative forms yellow needles, [196°].

(β)-*Compound* [206°]. Brownish-black microscopic crystals. Insol. aqueous NaOH, dissolves in H_2SO_4 to a blue solution. Sl. sol. alcohol, m. sol. chloroform (Wallach, *B.* 15, 2821).

Benzene-azo-oxy-cymene-azo-benzene

$\overset{(2)}{C_6H_5}-N_2-C_6\overset{(1)(4)(3)}{HMePr}(OH)-\overset{(5)}{N_2}-C_6H_5$. *Thymol-bi-diazo-benzene.* [168°]. Formed, together with benzene-azo-thymol, by the action of diazo-benzene on thymol (Mazzara, *G.* 15, 52, 228). Silky needles, sol. chloroform. By reduction with tin and HCl, and subsequent treatment with Fe_2Cl_6, it is converted into oxy-thymoquinone.

Benzene-azo-o-oxy-toluene-azo-benzene

$C_6H_5-\overset{(1)}{N_2}-C_6H_2\overset{(3)}{Me}\overset{(4)}{(OH)}-\overset{(5)}{N_2}-C_6H_5$. [115°]. Obtained by the action of (2 mols. of) diazo-benzene chloride on an alkaline solution of *o*-cresol (Nölting, *B.* 17, 364). Reddish-brown plates. V. sl. sol. cold alcohol. Dissolves in alkalis with a yellowish red colour.

Acetyl derivative [121°], yellow needles, v. sol. alcohol, ether, and benzene.

Benzene-azo-*m*-oxy-toluene-azo-benzene

$C_6H_5-\overset{(1)}{N_2}-C_6H_2\overset{(2)}{Me}\overset{(4)}{(OH)}-\overset{(3)}{N_2}-C_6H_5$. [149°]. Obtained by the action of (2 mols. of) diazo-benzene chloride on an alkaline solution of *m*-cresol. Reddish-brown plates. Sol. ether, benzene, and hot alcohol, sl. sol. cold alcohol.

Acetyl derivative [157°], small yellowish-brown needles (Nölting a. Kohn, *B.* 17, 367).

Benzene-azo-di-phenyl-urea azo-benzene

$C_6H_5-N_2-C_6H_4.NH.CO.NH.C_6H_4-N_2-C_6H_5$. [270°]. Formed by the action of carbonyl chloride on benzene-azo-aniline (Berju, *B.* 17, 1404; *C. C.* 1884, 871). Small plates. Sol. chloroform and benzene, sl. sol. alcohol.

Benzene-azo-di-phenyl-thio-urea-azo-benzene

$C_6H_5-N_2-C_6H_4.NH.CS.NH.C_6H_4-N_2-C_6H_5$. [199°]. Formed as a by-product of the action of phenyl-mustard oil on benzene-azo-aniline (Berju, *B.* 17, 1405). Sl. sol. hot chloroform, xylene, and acetic acid, v. sl. sol. alcohol, benzene, and CS_2.

Benzene-azo-pyrrol-azo-benzene

$C_6H_5-N_2-C_4H_2N-N_2-C_6H_5$,

probably
$C_6H_5.N_2.C=CH$
NH |
$C_6H_5.N_2.C=CH$
. [131°]. Obtained by combining (2 mols. of) diazo-benzene chloride with (1 mol. of) pyrrol in alkaline solution. Red crystalline solid. Sublimable. M. sol. ether and benzene, sl. sol. alcohol, nearly insol. water. Possesses basic properties. Dissolves in dilute HCl with a reddish-yellow colour; in conc. H_2SO_4 with a splendid blue colour. Its alcoholic solution is turned magenta-red by NaOH, reddish-violet by conc. HCl (O. Fischer a. Hepp, *B.* 19, 2251).

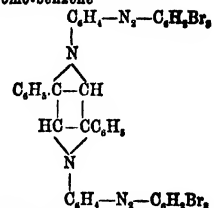
Benzene-azo-pyrrol-(β)-azo-naphthalene

$C_6H_5-N_2-C_4H_2N-N_2-C_{10}H_7$

probably
$C_6H_5.N_2.C=CH$
NH |
$C_{10}H_7.N_2C=CH$
. [151°]. Formed by the combination of diazo-benzene chloride with pyrrol-(β)-azo-naphthalene or of (β)-diazo-naphthalene chloride with pyrrol-azo-benzene, in alkaline alcoholic solution. Red plates, with bluish reflection. Sl. sol. alcohol (O. Fischer a. Hepp, *B.* 19, 2256).

Tri-bromo-benzene-azo-di-phenyl-di-isoindole-azo-tri-bromo-benzene

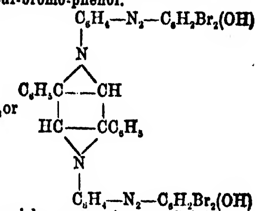
$C_{40}H_{24}N_8Br_6$ or



[150°]. Orange yellow prisms. Soluble in most ordinary solvents except water. Formed by the action of tri-bromo-diazo-benzene chloride on di-phenyl-di-iso-indole. — $B''H_2Cl_2$: slender yellowish-brown needles (Möhlau, *B.* 15, 2490).

Di-bromo-oxy-benzene-azo-di-phenyl-di-isoindole-azo-di-bromo-phenol.

$C_{40}H_{26}N_8Br_4O_2$ or



[198°]. Yellowish-green prisms. Soluble in alcohol, dyes wool orange and silk yellow. Formed by the action of di-bromo-diazo-phenol on di-phenyl-di-isoindole. — $B''H_2Cl_2$: short metallic glistening prisms, insol. water (Möhlau, *B.* 15, 2492).

ψ-Cumene-azo-*m*-di-oxy-benzene-azo-ψ-cumene

$C_6H_2Me_3-N_2-C_6H_2(OH)_2-N_2-C_6H_2Me_3$. Formed, together with cumene-azo-resorcin, by combining diazo-cumene chloride (from amido-pseudo-cumene [62°]) with resorcin (Liebermann a. Kostanecki, *B.* 17, 882). Small red needles. Dissolves in H_2SO_4 with a red colour. Insoluble in alkalis.

p-Di-methyl-amido-benzene-p-azo-benzene-azo-(β)-naphthol

$HO.C_{10}H_6-N_2-C_6H_4-N_2-C_6H_4.NMe_2$. [210°]. Got by pouring a diazotised solution of *p*-amido-benzene-azo-dimethylaniline hydrochloride into a solution of (β)-naphthol in NaOH (Meldola, *C. J.* 45, 109) Bronzy green needles. Sl. sol. alcohol, v. sol. hot $C_2H_4O_2$, benzene, and chloroform. Solutions in the above solvents are red; in alcoholic NaOH, red; in conc. H_2SO_4 green, turned blue by dilution. An alcoholic solution is turned blue by HCl.

p-Di-methyl-amido-benzene-p-azo-benzene-azo-(a)-naphthol

$HO.C_{10}H_6.N_2.C_6H_4.N_2.C_6H_4NMe_2$. Prepared like its ($\beta$) isomeride (M.). Its properties are similar, except that the solution in alcoholic KOH is violet. It decomposes below 200°.

Di-methyl-amido-benzene-azo-[illegible]-resorcin
$(HO)_2C_6H_3-N_2-C_6H_4-N_2-C_6H_4.NMe_2$. Brown powder. Decomposed before melting. Sl. sol. boiling alcohol, the solution being reddish-orange and turned first violet, then blue by adding HCl. Sl. sol. glacial acetic acid, the solution being red when hot, violet when cold. Insoluble in toluene. Solution in alcoholic KOH is reddish-violet. Solution in conc. H_2SO_4 is violet, becoming blue on dilution (Meldola, *C. J.* 45, 110).

Di-methyl-amido-benzene-*p*-azo-benzene-azo-phenol
$HO.C_6H_4-N_2-C_6H_4-N_2-C_6H_4NMe_2$. Brown powder, forming a brown solution in aqueous KOH, and a red solution in alcoholic KOH. Resembles the analogous di-methyl-amido-benzene-*p*-azo-benzene-azo-resorcin (*q. v.*) (Meldola, *C. J.* 45, 111).

Di-methyl-amido-benzene-azo-toluene-azo-(β)-naphthol
$\overset{(2)}{C_6H_4(NMe_2)}-N_2-\overset{(1)}{C_6H_3}\overset{(4)}{Me}-N_2-C_{10}H_6.OH$. From diazotised di-methyl-amido-benzene-azo-*p*-toluidine and (β)-naphthol (Wallach, *A.* 234, 358). Red needles (from chloroform), insol. water.

Di-methyl-amido-benzene-azo-toluene-azo-phenol
$\overset{(3)}{C_6H_4(NMe_2)}-N_2-\overset{(1)}{C_6H_3}\overset{(4)}{Me}-N_2-C_6H_4OH$. [160°]. From diazotised $C_6H_4(NMe_2)-N_2-C_6H_3MeNH_2$ and phenol (Wallach, *A.* 234, 357). Orange needles.

(α)-naphthalene-azo-pyrrol-(α)-azo-naphthalene $C_{10}H_7-N_2-C_4H_2NH-N_2-C_{10}H_7$,

$$\text{probably}\quad \begin{matrix} C_{10}H_7.N_2.C{=}CH \\ NH\,| \\ C_{10}H_7.N_2.C{=}CH \end{matrix}\ .$$

Formed by adding (α)-diazo-naphthalene chloride (2 mols.) to an alkaline solution of pyrrol (1 mol.). Metallic-glistening needles. Sol. alcohol with a dark yellowish-red colour. Dissolves in conc. H_2SO_4 with a blue colour (O. Fischer a. Hepp, *B.* 19, 2255).

(β)-Naphthalene-azo-pyrrol-(β)-azo-naphthalene $C_{10}H_7-N_2-C_4H_2NH-N_2-C_{10}H_7$.

$$\text{probably}\quad \begin{matrix} C_{10}H_7.N_2.C{=}CH \\ NH\,| \\ C_{10}H_7.N_2.C{=}CH \end{matrix}\ .\ [288°].$$

Formed by adding (β)-diazo-naphthalene chloride (2 mols.) to an alkaline solution of pyrrol (1 mol.). Glistening coppery plates. Sl. sol. alcohol. The alcoholic solution is turned reddish-violet by conc. HCl. Dissolves in conc. H_2SO_4 with a blue colour (O. Fischer a. Hepp, *B.* 19, 2255).

***m*-Nitro-benzene-*p*-azo-benzene-(α)-azo-(β)-naphthol** $NO_2C_6H_4-N_2-C_6H_4-N_2-C_{10}H_6.OH$. [c.218°]. From diazotised $NO_2.C_6H_4.N_2.C_6H_4.NH_2$ and (β)-naphthol. Small yield (Meldola, *C. J.* 45, 113). Orange crystals with green lustre. Solutions in $C_2H_4O_2$ and in toluene are orange; in alcoholic NaOH, violet; in conc. H_2SO_4 green, turned blue on dilution.

***m*-Nitro-benzene-(α)-azo-naphthalene-(α)-azo-(α)-naphthol**
$NO_2.C_6H_4-N_2-C_{10}H_6-N_2-C_{10}H_6.OH$. A dark amorphous powder. Solutions in toluene, chloroform and glacial acetic acid are red; in conc. H_2SO_4 dark indigo violet, becoming blue on dilution; in alcoholic potash, greenish-blue (Meldola, *C. J.* 45, 116).

***m*-Nitro-benzene-[illegible]-(α)-azo-(β)-naphthol**
$NO_2.C_6H_4-N_2-C_{10}H_6-N_2-C_{10}H_6.OH$. From *m*-nitro-benzene-(α)-azo-(α)-naphthylamine by diazotising and treating with (β)-naphthol (Meldola, *C. J.* 45, 115). Minute bronzy needles (from toluene). Blackens at 245°. Insol. alcohol or glacial acetic acid. Solutions in chloroform and in hot aniline are violet; in toluene red when hot, reddish-violet when cold; in boiling alcoholic KOH, blue; in conc. H_2SO_4, olive colour, on dilution, blue and then violet.

***m*-nitro-benzene-(α)-azo-naphthalene-azo-resorcin** $NO_2.C_6H_4-N_2-C_{10}H_6-N_2-C_6H_3(OH)_2$. Bronzy powder, not very soluble. Solutions in boiling alcohol are reddish; in glacial acetic acid, toluene and chloroform, orange; in aqueous or alcoholic KOH, blue; in conc. H_2SO_4, green, changing to bluish-green on dilution (Meldola, *C. J.* 45, 116).

***p*-Nitro-benzene-azo-*m*-xylene-azo-(α)-naphthol** $NO_2.C_6H_4-N_2-C_6H_2Me_2-N_2-C_{10}H_6.OH$. Preparation and properties are similar to those of the preceding (β)-compound.

Sulphonic acid
$NO_2C_6H_4-N_2-C_6H_2Me_2-N_2-C_{10}H_5(SO_3H)(OH)$ Similar to the corresponding (β)-compound, but dyes reddish-brown.

***p*-Nitro-benzene-azo-*m*-xylene-azo-β-naphthol**
$NO_2.C_6H_4-N_2-C_6H_2Me_2-N_2-C_{10}H_6.OH$. [278°]. From $NO_2.C_6H_4-N_2-C_6H_2Me_2NH_2$ by diazotising and treating with sodium (β)-naphthol (Meldola, *C. J.* 43, 434). Green scales (from toluene). Scarcely soluble in alcohol or glacial acetic acid. Forms a crimson solution in boiling aniline or nitrobenzene, and a green solution in conc. H_2SO_4, turned violet by dilution.

Sulphonic acid
$NO_2.C_6H_4.N_2.C_6H_2Me_2.N_2.C_{10}H_5(OH)SO_3H$. Got by using $C_{10}H_6(OH)SO_3H$. Dyes claret-red.

***p*-Nitro-benzene-azo-*m*-xylene-azo-phenol**
$NO_2.C_6H_4-N_2-C_6H_2Me_2-N_2-C_6H_4.OH$. Orange powder. Sl. sol. alcohol and benzene, v. sol. hot aniline. Solutions are orange. Solution in alcoholic NaOH is reddish-violet. Solution in conc. H_2SO_4 is blue (Meldola, *C. J.* 43, 436).

***p*-Nitro-benzene-azo-*m*-xylene-azo-resorcin**
$NO_2.C_6H_4-N_2-C_6H_2Me_2-N_2-C_6H_3(OH)_2$. [231°]. Brown powder. Forms orange solutions in boiling alcohol, toluene, and glacial acetic acid. Solution in alcoholic NaOH is red, turned violet by excess of NaOH. Conc. H_2SO_4 forms a blue solution (Meldola, *C. J.* 43, 436).

***p*-Oxy-benzene-*p*-azo-benzene-(α)-azo-(α)-naphthol** $C_6H_4(OH)-N_2-C_6H_4-N_2-C_{10}H_6.OH$. From diazotised *p*-amido-benzene-azo-(α)-naphthol and an alkaline solution of phenol (Meldola, *C. J.* 47, 665). Dark amorphous powder. Its solution in conc. H_2SO_4 is indigo-blue; in boiling toluene, orange; in alcohol, red; in KOHAq, dull red; and in alcoholic NaOH, deep claret colour.

***p*-Oxy-benzene-*p*-azo-benzene-(α)-azo-(β)-naphthol** $HO.C_6H_4-N_2-C_6H_4-N_2-C_{10}H_6(OH)$. [225°]. From *p*-amido-benzene-azo (β)-naphthol by diazotising and mixing with an alkaline solution of phenol (Meldola, *C. J.* 47, 666). Red warty concretions. Its solution in conc. H_2SO_4 is bluish-green, and becomes violet on dilution.

Its solution in boiling toluene, or boiling alcohol, is red. Its solution in KOHAq is reddish-violet.

***m*-Di-oxy-benzene-*p*-azo-benzene-(α)-azo-(α)-naphthol**
[4:2:1] $C_6H_3(OH)_2—N_2—C_6H_4—N_2—C_{10}H_6(OH)$. Formed by mixing diazotised *p*-amido-benzene-azo-(α)-naphthol with a solution of resorcin in dilute NaOH (Meldola, *C. J.* 47, 665). Bronzy-green powder; sl. sol. toluene and acetic acid, forming a red solution. Its solution in KOHAq is blue; its solution in NH_3Aq is violet. It is decomposed by heat without fusion.

***m*-Di-oxy-benzene-*p*-azo-benzene-(α)-azo-(β)-naphthol**
[4:2:1] $C_6H_3(OH)_2—N_2—C_6H_4—N_2—C_{10}H_6.OH$. From diazotised *p*-amido-benzene-azo-(β)-naphthol and an alkaline solution of resorcin (Meldola, *C. J.* 47, 666). Bronzy-green powder. Its solution in conc. H_2SO_4 is deep bluish-green; in dilute aqueous alkalis, violet. Sl. sol. toluene forming a red solution.

***m*-Oxy-benzene-azo-benzene-*p*-azo-phenol**
[3:1] $HO.C_6H_4—N_2—C_6H_4—N_2—C_6H_4.OH$ [1:4]. Dark powder. Easily soluble in alkalis. Formed by diazotising amido-benzene-*m*-azo-phenol ($C_6H_4(OH)—N_2—C_6H_4.NH_2$) and combining it with phenol (Wallach a. Schulze, *B.* 15, 3021).

***p*-Oxy-benzene-azo-benzene-*p*-azo-phenol**
[4:1] $HO.C_6H_4—N_2—C_6H_4—N_2—C_6H_4.OH$ [1:4]. [c. 207°]. From diazotised amido-benzene-*p*-azo-phenol and a solution of phenol in dilute alkali (Meldola, *C. J.* 47, 660). Amorphous brown powder. Its solution in conc. H_2SO_4 is violet, unchanged on considerable dilution; v. sol. NH_3Aq and KOHAq forming a red solution; insol. boiling toluene; forms an orange solution in hot phenol or aniline.

***m*-Di-oxy-benzene-*p*-azo-benzene-azo-resorcin**
[4:2:1] $C_6H_3(OH)_2—N_2—C_6H_4—N_2—C_6H_3(OH)_2$ [1:2:4]. From diazotised *p*-amido-benzene-azo-resorcin and an alkaline solution of resorcin (Meldola, *C. J.* 47, 661). Dull bronze-like powder, v. sl. sol. alcohol, insol. toluene. Its solutions in conc. H_2SO_4 and in alkalis are violet.

Oxy-carboxy-benzene-azo-benzene-(α)-azo-(β)-naphthol
$$C_6H_3\overset{(4)}{(CO_2H)}\overset{(3)}{(OH)}\overset{(1)}{—N_2—}C_6H_4\overset{(1)(\alpha)}{—N:N—}C_{10}H_6\overset{(\beta)}{(OH)}.$$
[above 255°]. From diazotised *p*-amido-benzene-azo-salicylic acid and an alkaline solution of (β)-naphthol (Meldola, *C. J.* 47, 668). Minute brown needles (from boiling aniline). V. sl. sol. boiling toluene, sl. sol. alcohol and glacial HOAc. Its solution in conc. H_2SO_4 is greenish-blue, changing to violet on dilution. Its solution in KOHAq is reddish-violet.

Oxy-cymene-azo-tri-phenyl-methane-azo-thymol
$$\begin{array}{l}[6:3:4:1]\,C_6H_2MePr(OH)—N_2—C_6H_4 \\ [6:3:4:1]\,C_6H_2MePr(OH)—N_2—C_6H_4\end{array}>CHPh.$$
[170°]. Formed by mixing diazotised diamido-tri-phenyl-methane hydrochloride with an alkaline solution of thymol (Mazzara, *G.* 15, 44). Amorphous black powder. After reduction and oxidation it gives thymoquinone.

(α)-Oxy-naphthalene-*p*-azo-benzene-(α)-naphthol
$$C_{10}H_6\overset{(\alpha)}{(OH)}\overset{(\alpha)(4)}{—N:N—}C_6H_4\overset{(1)(\alpha)}{—N:N—}C_{10}H_6\overset{(\alpha)}{(OH)}.$$
Formed by diazotising *p*-amido-benzene-azo-(α)-naphthol and mixing the product with an alkaline solution of (α)-naphthol (Meldola, *C. J.* 47, 664). Green lustrous powder; v. sl. sol. glacial HOAc, alcohol, and toluene, m. sol. boiling aniline, forming a red solution. Its solution in NaOHAq is blue, in conc. H_2SO_4 blue, turned violet on dilution. With Ac_2O and NaOAc it forms on heating a di-acetyl derivative.

(β)-Oxy-(α)-naphthalene-*p*-azo-benzene-(α)-azo-(β)-naphthol
$$C_{10}H_6\overset{(\beta)}{(OH)}\overset{(\alpha)(1)}{—N:N—}C_6H_4\overset{(4)(\alpha)}{—N:N—}C_{10}H_6\overset{(\beta)}{(OH)}.$$
[over 275°]. From diazotised *p*-amido-benzene-azo-(β)-naphthol and an alkaline solution of (β)-naphthol (Meldola, *C. J.* 47, 664). Dull bronzy powder, or green needles (from hot aniline). Insol. boiling alcohol, or NaOHAq; sol. cold alcoholic NaOH, forming a violet solution. Sl. sol. hot toluene forming a magenta solution. Conc. H_2SO_4 forms a blue solution, turned violet on dilution.

(α)-Oxy-naphthalene-*p*-azo-benzene-azo-(β)-naphthol
$$C_{10}H_6\overset{(\alpha)}{(OH)}\overset{(\alpha)(1)}{—N:N—}C_6H_4\overset{(4)(\alpha)}{—N:N—}C_{10}H_6\overset{(\beta)}{(OH)}.$$
[236°]. From diazotised *p*-amido-benzene-azo-(α)-naphthol and an alkaline solution of (β)-naphthol (Meldola, *C. J.* 47, 665). Dull bronzy powder, v. sl. sol. boiling alcohol; m. sol. boiling toluene and glacial acetic acid forming violet solutions; conc. H_2SO_4 forms a blue solution, becoming violet on dilution.

(α)-Oxy-naphthalene-*p*-azo-benzene-azo-(β)-naphthol-di-sulphonic acid
$$C_{10}H_6\overset{(\alpha)}{(OH)}\overset{(\alpha)(1)}{—N:N—}C_6H_4\overset{(4)}{—N:N—}C_{10}H_4(SO_3H)_2\overset{(\beta)}{(OH)}.$$
From diazotised *p*-amido-benzene-azo-(α)-naphthol and an alkaline solution of (β)-naphthol di-sulphonic acid. Its sodium salt is violet and gelatinous; it is an indigo-blue dye (Meldola, *C. J.* 47, 665).

(β)-Oxy-naphthalene-azo-benzene-azo-(β)-naphthol di-sulphonic acid. Is similar to the last body, but of greater stability (M.).

Oxy-di-sulpho-naphthalene-azo-benzene-azo-(β)-naphthol di-sulphonic acid
$C_{10}H_4(SO_3H)_2(OH)—N_2—C_6H_4—N_2—C_{10}H_4(SO_3H)_2(OH)$. Glistening greenish needles. Dyes wool and silk a deep indigo-blue, which, however, is very unstable to light. Is prepared by diazotising the mono-acetyl derivative of *p*-phenylene-diamine and combining it with (β)-naphthol-di-sulphonic acid (modification insoluble in spirit), the product $C_6H_4(NHAc).N_2.C_{10}H_4(OH)(SO_3H)_2$, which is a scarlet colouring matter, is saponified, diazotised, and again combined with (β)-naphthol-di-sulphonic acid (Nietzki, *B.* 17, 344; 1350).

Phenyl-amido-benzene *p*-azo-benzene-azo-(β)-naphthol
$HO.C_{10}H_6—N_2—C_6H_4—N_2—C_6H_4NHC_6H_5$. [204°]. From *p*-amido-benzene-azo-di-phenyl-amine by diazotising and adding sodium (β)-naphthol (Meldola, *C. J.* 43, 442). Warty scales with bronze lustre. Sl. sol. boiling alcohol, v. sol. benzene. The solutions are red. In glacial acetic acid the solution is red when hot, violet when cold. Solution in conc. H_2SO_4 is greenish-blue, solution in alcoholic KOH is red but turned blue by HCl (characteristic).

Phenyl-ethyl-amido-benzene-azo-benzene-azo-(β)-naphthol
$HO.C_{10}H_6—N_2—C_6H_4—N_2—C_6H_4.NEt.C_6H_5.$

From *p*-diazo-nitro-benzene by combining with ethyl-di-phenyl-amine, reducing with ammonium sulphide, diazotising the product and treating with (β)-naphthol. Bronzy powder. Solutions in alcoholic KOH, alcohol, and benzene are red; in conc. H_2SO_4 indigo-blue, turned bright blue on diluting. HCl turns the alcoholic solution blue (Meldola, *C. J.* 45, 111).

***p*-Sulpho-benzene-azo-benzene-azo-(β)-naphthol-(β)-sulphonic acid**

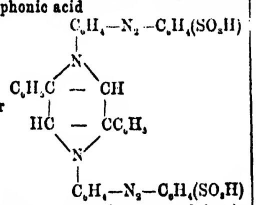
$$\overset{(4)}{C_6H_4}(SO_3\overset{(1)}{H})-\overset{(1)}{N}:N-\overset{(4)(\alpha)}{C_6H_4}-N:N-C_{10}H_5(\overset{(\beta)}{SO_3H})(\overset{(\beta)}{OH}).$$

From diazotised *p*-amido-benzene-azo-benzene sulphonic acid and an ammoniacal solution of sodium (β)-naphthol 'α'-sulphonic acid (Bayer a. Co., *B.* 15, 1351). The sodium salt is a scarlet dye (croceïne scarlet). Conc. H_2SO_4 forms a blue solution. The absorption spectrum has been studied by Hartley (*C. J.* 51, 195).

***p*-Sulpho-benzene-azo-benzene-azo-tolylene diamine**

$C_6H_4(SO_3H)-N_2-C_6H_4-N_2-C_7H_5(NH_2)_2$. Reddish-brown microscopic needles. Formed by combining diazo-benzene-azo-benzene-*p*-sulphonic acid with tolylene-diamine (Griess, *B.* 16, 2036).

Sulpho-benzene-azo-di-phenyl-di-isoindole-azo-benzene sulphonic acid

$C_{40}H_{28}N_6S_2O_6$ or 

Formed by the action of diazo-benzene-sulphonic acid on di-phenyl-di-isoindole. Metallic glistening brown scales. Very slightly soluble in all solvents. Dyes silk and wool nearly the same shade as chrysoïdine. On reduction it gives sulphanilic acid and di-amido-di-phenyl-di-isoindole.

Salts.—$A''Na_2aq$: yellow plates.—$A''Ag_2$: red prisms (Möhlau, *B.* 15, 2495).

Sulpho-benzene-azo-sulpho-benzene-(α)-azo-(β)-naphthol

$C_6H_4(SO_3H)-N_2-C_6H_3(SO_3H)-N_2-C_{10}H_6.OH$. From diazo-sulpho-benzene-azo-benzene sulphonic acid and an alkaline solution of (β)-naphthol (Nietzki, *B.* 13, 800). The sodium salt is a red dye (*Biebrich scarlet*). Conc. H_2SO_4 forms a green solution. Its absorption spectrum has been studied by Hartley (*C. J.* 51, 194).

Sulpho-benzene-azo-sulpho-benzene-(β)-azo-naphthyl-*p*-tolyl-amine ('*Wool-black*')

$C_6H_4(SO_3H).N_2.C_6H_3(SO_3H).N_2.C_{10}H_6.NHC_7H_7$. The coml. product is a bronzy powder. V. sol. hot water with a violet-blue colour. Dissolves in conc. H_2SO_4 with a deep indigo-blue colour. Formed by combination of diazotised amido-sulpho-benzene-azo-benzene-sulphonic acid with *p*-tolyl-(β)-naphthylamine. By boiling with moderately dilute H_2SO_4 it is decomposed into tolu-(αβ)-naphthazine [169°] and amidoazo-benzene-di-sulphonic acid:

$$C_6H_4(SO_3H)-N_2-C_6H_3(SO_3H)-N_2-C_{10}H_6.NHC_7H_7 = C_{10}H_6\langle N_2 \rangle C_7H_6 + C_6H_4(SO_3H)-N_2-C_6H_3(NH_2)(SO_3H).$$

The Ca and Ba salts are insoluble black pps. (Witt, *B.* 20, 579).

***p*-Toluene-azo-*m*-diamido-benzene-azo-(β)-naphthalene** $C_7H_7-N_2-C_6H_2(NH_2)_2-N_2-C_{10}H_7$. Formed by the combination of *p*-diazo-toluene with (β)-naphthalene-azo-*m*-phenylene-diamine (Griess, *B.* 16, 2031). Small red glistening plates. V. sol. chloroform.

***p*-Toluene-azo-ethyl-pyrrol-*p*-azo-toluene** $C_7H_7-N_2-C_4H_2NEt-N_2-C_7H_7$,

$$\text{probably}\quad \begin{array}{l} C_6H_4Me.N_2.C{=}CH \\ \qquad\qquad NEt| \\ C_6H_4Me.N_2.C{=}CH \end{array} \quad [180°].$$

Formed by ethylation of toluene-azo-pyrrol-azo-toluene; or by combining diazo-*p*-toluene chloride (2 mol.) with ethyl-pyrrol (1 mol.) in alkaline solution. Steel-blue needles. Sl. sol. alcohol (O. Fischer a. Hepp, *B.* 19, 2254).

Toluene-azo-dioxy-benzene-azo-toluene

$C_7H_7-N_2-C_6H_2(OH)_2-N_2-C_7H_7$. By the action of *p*-diazotoluene chloride on an alkaline solution of *p*-toluene-azo-resorcin two isomerides are formed which are separated by their different solubilities in alkalis.

(α)-*Compound* [256°]. Yellow felted needles. Sparingly soluble in alcohol and cold chloroform.

(β)-*Compound* [203°]. Brownish-black microscopic needles (Wallach, *B.* 15, 2825).

Toluene-azo-trioxybenzene-azo-toluene

$C_6H_4Me-N_2-C_6H(OH)_3-N_2-C_6H_4Me$. Long red needles. Prepared by the action of diazotoluene nitrate on phloroglucin (Weselsky a. Benedikt, *B.* 12, 227).

Toluene-azo-pyrrol-azo-toluene

$C_7H_7-N_2-C_4H_2NH-N_2-C_7H_7$,

$$\text{probably}\quad \begin{array}{l} C_6H_4Me.N_2.C{=}CH \\ \qquad\qquad NH| \\ C_6H_4Me.N_2.C{=}CH \end{array} \quad . \ [179°].$$

Formed by adding (2 mols.) diazo-*p*-toluene chloride to an alkaline solution of pyrrol (1 mol.). Red prisms with steel-blue reflex. Sl. sol. alcohol. Its alcoholic solution is turned reddish-violet by conc. HCl. Dissolves in conc. H_2SO_4 with a blue colour (O. Fischer a. Hepp, *B.* 19, 2254).

Toluene-*o*-azo-toluene-azo-(α)-naphthol

$$\overset{(4)}{C_6H_4}(CH_3)-\overset{(1)}{N_2}-\overset{(5)}{C_6H_3}(CH_3)-\overset{(2)}{N_2}-C_{10}H_6(\overset{(\alpha)}{OH}),$$

$$\text{or}\ C_6H_3(CH_3)\begin{cases} N-N-C_{10}H_6(OH) \\ \ |\quad\ \ | \\ N-N-C_6H_4(CH_3) \end{cases} . \ [210°].$$

Formed by combination of *o*-diazo-azo-toluene with (α)-naphthol. Brownish-red needles (from aniline). Sl. sol. ordinary solvents. Insol. aqueous NaOH, sol. alcoholic NaOH with a violet-red colour. By $SnCl_2$ it is slowly reduced to amido-(α)-naphthol and tolyl-azimido-toluene $C_7H_6{:}N_2.C_7H_7$, together with small quantities of *p*-toluidine and tolylene-*o*-diamine (Zincke a. Lawson, *B.* 20, 1178).

Toluene-*o*-azo-toluene-azo-(β)-naphthol

$$\overset{(4)}{C_6H_4}(CH_3)-\overset{(1)}{N_2}-\overset{(5)}{C_6H_3}(CH_3)-\overset{(2)}{N_2}-C_{10}H_6(\overset{(\beta)}{OH}),\ \text{or}$$

$$C_6H_3(CH_3)\begin{cases} N-N-C_{10}H_6(OH) \\ \ |\quad\ \ | \\ N-N-C_6H_4(CH_3) \end{cases} . \ [177°].$$

Formed by combination of *o*-diazo-azo-toluene with (β)-naphthol. Long dark-red four-sided prisms, with green reflex. V. sol. benzene, and chloroform, sl. sol. alcohol, acetone, and petroleum-spirit. Dissolves in alcoholic NaOH only slightly.

By $SnCl_2$ it is reduced to (α)-amido-(β)-naphthol and tolyl-azimido-toluene $C_7H_6{:}N_3{.}C_7H_7$, together with small quantities of *p*-toluidine and tolylene-*o*-diamine (Zincke a. Lawson, *B.* 20, 1179).

Toluene-*p*-azo-toluene-azo-β-naphthol

$\overset{(2)}{C_6H_4}(\overset{(1)}{CH_3})-N_2-\overset{(3)}{C_6H_3}(\overset{(4)}{CH_3})-N_2-C_{10}H_6(\overset{(\beta)}{OH})$. [186°]. Formed by combination of *p*-diazo-azo-toluene with (β)-naphthol. Deep-red needles. V. sol. hot alcohol and benzene. By $SnCl_2$ it is easily reduced, giving (α)-amido-(β)-naphthol, *o*-toluidine, and tolylene-*p*-diamine $C_6H_3Me(NH_2)_2$ [1:2:5] (Zincke a. Lawson, *B.* 20, 1182).

Toluene-*o*-azo-toluene-azo-(β)-naphthylamine $\overset{(4)}{C_6H_4}(\overset{(1)}{CH_3}).N_2.\overset{(5)}{C_6H_3}(\overset{(2)}{CH_3}).N_2.C_{10}H_6(\overset{(\beta)}{NH_2})$, or the corresponding hydrazimido-formula. [203°]. Formed by combination of *o*-diazo-toluene-azo-toluene with (β)-naphthylamine. Deep-red glistening plates. V. sol. benzene and chloroform. By $SnCl_2$ it is reduced to tolyl-azimido-toluene $C_7H_6{:}N_3C_7H_7$ and (probably) naphthylene-*o*-diamine (Zincke a. Lawson, *B.* 20, 1180).

AZO- COMPOUNDS, TERTIARY.

Oxy-benzene-*p*-azo-benzene-(α)-azo-naphthalene-azo-phenol

$HO.C_6H_4-N_2-C_6H_4-N_2-C_{10}H_6-N_2-C_6H_4.OH.$
From $NH_2.C_6H_4-N_2-C_{10}H_6.NH_2$ by diazotising and adding sodic phenate (Meldola, *C. J.* 43, 439). Dull bronzy-green powder. Forms orange solutions with boiling aniline or toluene. Solution in alcoholic KOH is violet; in conc. H_2SO_4, indigo-blue.

Di-oxy-benzene-*p*-azo-benzene-(α)-azo-naphthalene-azo-resorcin

$(HO)_2C_6H_3-N_2-C_6H_4-N_2-C_{10}H_6-N_2-C_6H_3(OH)_2$.
Brown powder. Its solutions are dull red in alcohol, violet in alcoholic KOH, bluish-green in conc. H_2SO_4.

(β)-oxy-naphthalene-*p*-azo-benzene-(α)-azo-naphthalene-azo-(β)-naphthol

$HO.C_{10}H_6-N_2-C_6H_4-N_2-C_{10}H_6-N_2-C_{10}H_6.OH.$
Formed by diazotising amido-benzene-azo-(β)-naphthylamine $NH_2.C_6H_4.N_2.C_{10}H_6.NH_2$ and treating with an alkaline solution of (β)-naphthol (Meldola, *C. J.* 43, 437). The pp. may be separated by crystallisation from hot aniline into two modifications, one remaining in solution, the other separating as needles with green lustre.

Crystalline form [c. 295°]. Insoluble in boiling alcohol, acetone, or glacial acetic acid, hardly soluble in chloroform or benzene. Forms violet solutions with aniline or nitrobenzene. Solution in conc. H_2SO_4 is deep inky blue. Alcoholic KOH forms, with difficulty, a blue solution.

Soluble form.—Soluble in the above liquids. Its solution in boiling glacial acetic acid is violet when hot, blue when cold. Solution in conc. H_2SO_4 is clear indigo-blue. Alcoholic potash forms a violet solution.

Di-sulphonic acid.—From (β)-naphthol-sulphonic acid and diazotised $NH_2.C_6H_4.N_2.C_{10}H_6.NH_2$.

(α)-Oxy-naphthalene-*p*-azo-benzene-(α)-azo-naphthalene-azo-(α)-naphthol. Similar to the preceding. Bronzy powder, forming a blue solution in alcoholic KOH, and an indigo-blue solution with conc. H_2SO_4.

(β)-Oxy-naphthalene-*p*-azo-xylene-azo-(β)-naphthol

$HO.C_{10}H_6-N_2-C_6H_4-N_2-C_6H_2Me_2-N_2-C_{10}H_6OH.$
From $NH_2.C_6H_4.N_2.C_6H_2Me_2NH_2$ by diazotising and adding sodium (β)-naphthol (Meldola, *C. J.* 43, 439). Small green needles (from xylene). Its solution in aniline is reddish-violet; in xylene, violet; in hot alcoholic KOH, bluish-violet; in conc. H_2SO_4 greenish-blue, becoming blue on dilution. It is insoluble in alcohol and in glacial acetic acid. Its sulphonic acid dyes silk and wool dull violet.

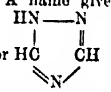
Tri-oxy-tri-naphthalene-hexa-azo-tri-phenyl-carbinol $HO.C(C_6H_4-N_2-C_{10}H_6OH)_3$. From diazotised para-rosaniline and (α)- or (β)-naphthol in alkaline solution (Meldola, *C. J.* 47, 668). Orange amorphous powders. Similar compounds may be got from ordinary rosaniline. They dye silk and wool orange.

AZO- COTTON DYES. The azo- dye-stuffs obtained from benzidine and its homologues (Congo-red, benzopurpurine, deltapurpurine, benzaurine, chrysamine, benzazurine, &c.) have the special characteristic of dyeing cotton without a mordant. This property depends upon the constitution of the diphenyl molecule, for benzidine itself (and other diphenyl bases) readily combines with the cotton fibre. This is easily shown by allowing cotton to soak for 24 hours in a cold solution of benzidine hydrochloride, wringing, drying at the ordinary temperature, and washing thoroughly with hot and cold water; if the cotton thus mordanted with benzidine is now passed through a dilute solution of nitrous acid, and finally treated with a solution of (α)-naphthylamine-sulphonic acid it becomes dyed with Congo-red (Möhlau, *B.* 19, 2014).

Tetrazo-diphenyl (diazotised benzidine) forms red dye-stuffs by combination with (α)- and (β)-mono-sulphonic acids of (β)-naphthol or with the G di-sulphonic acid. The R di-sulphonic acid (Na salt insoluble in spirit) however exhibits a very peculiar reaction. One mol. of tetrazo-diphenyl combines with one mol. of the R di-sulphonate forming a dye-stuff which is red. If two mols. of the sulphonate are taken one mol. remains in solution unused. If now the ppd. red colouring matter is heated with the mother liquor, the second mol. of di-sulphonate is taken up and a blue colouring matter is produced. A similar reaction has been observed with many other di-amido- bodies (Schultz, *B.* 17, 461).

In general, the tetrazo- derivatives of diphenyl, ditolyl, &c. (obtained by diazotising benzidine and its homologues) can combine with either one or two mols. of a phenol, amine, or their sulphonic and carboxylic acids. The compounds with one mol., viz., $R''\!<\!\begin{smallmatrix}N_2.OH\\N_2.R'\end{smallmatrix}$, are tolerably stable, and sparingly soluble; by boiling with water or with alcohol the uncombined diazo- group is replaced by OH or by hydrogen. These half-conjugated diazo- compounds readily combine with a second mol. of phenol or amine, so that mixed azo-compounds can be thus obtained. The latter bodies are colouring-matters of various shades, and dye cotton direct without a mordant (Lange, *B.* 19, 1697; Martius, *B.* 19, 1755).

The azo-compounds (Hessian yellow, Hessian purple, curcumine, &c.) obtained by combining two mols. of a phenol, amine or respective sulphonic acid, or one mol. of one amine or phenol and one mol. of another, with the tetrazo-compound derived from di-*p*-amido-di-phenyl-ethylene or its sulphonic acids, have the property of dyeing unmordanted cotton from a soap-bath. The compound from (α)-naphthol-sulphonic acid dyes cotton a bluish-violet, (β)-naphthol-R-di-sulphonic acid a blue, (α)-naphthylamine-sulphonic acid a red salicylic acid a yellow, &c. (Bender a. Schultz, *B.* 19, 3234). The di-amido-derivatives of fluorene also give colouring matters which dye cotton. To the class of cotton colours also belongs the compound which has recently been introduced under the name of 'Primuline.' This body dyes unmordanted cotton from an alkaline bath a greenish yellow. It is an amido- compound and may be diazotised upon the fibre. By treatment of the cotton thus prepared with solutions of amines or phenols, fast colours (red, orange, and brown) may be produced (Green, *priv. com.*).

TRIAZOL. A name given to the hypothetical $C_2H_3N_3$ or 
(Bladin, *B.* 19, 2598) (*v.* PHENYL-METHYL-TRIAZOL and CYANO-PHENYL METHYL-TRIAZOL).

AZO-MECONIC-ACETIC ACID *v. Dioxy-carboxy-methyl-phthalide*-AZO-*dioxy-phthalide-acetic acid.*

AZO-DI-METHYL-HYDROQUINONE *v. Di-oxy-benzene*-AZO-*hydroquinone.*

AZO-NAPHTHALENE *v. Naphthalene*-AZO-*naphthalene.*

TETRAZONES. Compounds of the form $R_2:N.N:N.N:R_2$ obtained by oxidising unsymmetrical di-alkylated *hydrazines* (*q. v.*).

AZONIUM BASES. Compounds of the form $NH_2.NRR'R''(OH)$ (Fischer). The name has been also applied by Witt (*B.* 20, 1183) to compounds of the form $X''\!<\!\begin{matrix} NR'(OH) \\ | \\ N \end{matrix}\!>\!Y''$.

AZO-OPIANIC ACID is amido-hemipic anhydride, *v.* HEMIPIC ACID.

AZOPHENINE $C_{36}H_{29}N_5$. [237°]. Is formed by the action of a variety of azo- and nitroso-compounds (*e.g.* benzene-azo-aniline, toluene-azo-toluidine, phenyl-amido-benzene-azo-benzene, chrysoidine, diphenyl-nitrosamine, nitroso-di-methyl-aniline, &c.) upon aniline (Kimich, *B.* 8, 1026). The best method of preparation consists in warming an acetic acid solution of aniline with a nitroso- compound (*e.g.* nitroso-di-methyl-aniline) filtering off the crystals of azophenine, washing them with alcohol and re-crystallising from aniline or nitro-benzene. If the aniline is replaced by its homologues, the homologues of azophenine are obtained. It forms unstable salts of violet colour. It cannot be acetylated. Conc. H_2SO_4 at 100° yields a sulphonic acid crystallising in violet needles, which form brown crystalline salts. By heating with aniline hydrochloride it is converted into induline (*q. v.*). By heating alone at 360° it is converted into aniline, a violet intermediate body, and fluorindine. The latter is a splendid blue crystalline colouring-matter, the solutions of which have a beautiful red fluorescence and a characteristic absorption spectrum. By reduction with $SnCl_2$ azophenine yields aniline and a sparingly soluble hydrochloride of an unstable base. The latter, when set free by alkalis, rapidly absorbs oxygen from the air, and changes into a new colouring-matter, the salts of which are indigo-blue (Witt, *B.* 20, 1538; Witt a. Thomas, *C. J.* 43, 112).

AZO-PHENYL ACETIC ACID *v. Exo-carboxy-toluene*-AZO-*phenyl-acetic acid.*

AZO-DIPHENYL BLUE *v.* INDULINE.

AZO-PHENYLENE, now called PHENAZINE (*q. v.*).

AZO-PHTHALIC ACID *v. Di-carboxy-benzene*-AZO-*phthalic acid.*

AZO-PYROMELLITIC ACID $C_6N_2(CO_2H)_4$.

Tetra-ethyl ether $A^{iv}Et_4$ [134°]; glistening red trimetric tables; easily soluble in alcohol, ether, and acetic acid, insoluble in water; sublimable. Formed by reduction of di-nitro-mellitic ether with zinc-dust and acetic acid. It forms an unstable colourless hydrochloride (Nef, *B.* 18, 2805).

AZO-RESORCIN *v.* RESORCIN.

AZO-RESORUFIN *v.* RESORCIN.

AZO-TOLUENE *v. Toluene*-AZO-*toluene.*

AZO-TOLUIDINE *v. Amido-toluene*-AZO-*toluidine.*

AZOXIMS. Amidoxims, $R.C(NOH).NH_2$, are produced by the union of hydroxylamine with nitriles; these react with acid chlorides, $R'.CO.Cl$, or anhydrides, $(R'CO)_2O$, with formation of alkoyl derivatives, $R.C(NO.CO.R').NH_2$, which under suitable conditions (application of heat, or boiling with water) split off water and change into azoxims $R.C\!<\!\begin{matrix} N.O \\ N \end{matrix}\!>\!C.R'$. The azoxims are very volatile in the vapour of other liquids or in air; many of those boiling above 200° are volatile even in vapour of ether. They sublime at the ordinary temperature of the air (Tiemann, *B.* 18, 1060; 19, 1475).

Chloroformic ether acting upon benzamidoxim produces an azoxim which has the character of a lactam, $C_6H_5.C\!<\!\begin{matrix} N.O \\ NH \end{matrix}\!>\!CO$.

Phenyl-acet-amidoxim,

$$Ph\,CH_2.C(NOH).NH_2,$$

does not produce azoxims so readily as benz-amidoxim, $Ph.C(NOH).NH_2$, but phenyl-acryl-amidoxim (cinnamidoxim), $Ph.CH:CH.C(NOH).NH_2$, produces them with great ease.

m-**Amido-benzenyl-azoxim-benzenyl**

$C_6H_4(NH_2).C\!<\!\begin{matrix} N.O \\ N \end{matrix}\!>\!C.C_6H_5$. [143°]. Formed by reduction of *m*-nitro-benzenyl-azoxim-benzenyl with alcoholic ammonium sulphide. Crystallises from alcohol or sublimes in long needles. V. sol. alcohol, ether, benzene, and chloroform, insol. ligroïn and water. By nitrous acid it is diazotised.

Salts.—B'HCl: very sparingly soluble.—$B'_2H_2Cl_2PtCl_4$: sparingly soluble pp.

Benzoyl derivative $C_{14}H_9ON_3(NHBz)$: [213°]; needles; sol. boiling alcohol, ether, and benzene, insol. water and ligroïn (Schöpff, *B.* 18, 2473).

Benzenyl-azoxim-benzenyl $C_{14}H_{10}N_2O$ *i.e.* $C_6H_5.C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.C_6H_5$. [108°]. (290°). Volatile with steam. Sublimes in long white needles. V.D. (H = 1) 113·3. V. sol. alcohol, ether, and benzene; v. sl. sol. water.

Formation.—1. By heating the benzoyl derivative of benz-amidoxim $C_6H_5.C(NH_2):N.OBz$. 2. By heating benz-amidoxim with benzoic acid, or with benzotrichloride.

Reactions.—It is an extremely stable substance, being unattacked even by strong HNO_3 or H_2SO_4. Long boiling with tin and HCl reduces it to benzonitrile (Tiemann a. Krüger, *B.* 17, 1694).

Benzenyl-azoxim-benzenyl-*o*-carboxylic acid $C_6H_5.C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.C_6H_4.CO_2H$. [151°]. Formed by melting together benz-amidoxim and phthalic anhydride. White glistening needles. V. sol. alcohol, ether, and benzene, v. sl. sol. water and ligroïn.

Salts.—A′Ag: white crystalline pp.—A'_2Ba 4aq: plates or microscopic needles.—A'_2Cu: bluish-green pp.—A′PbOH: white granular pp.

Ethyl ether.—A′Et: heavy yellow oil.

Amide.—$C_{14}H_9ON_2.CONH_2$: [160°], microscopic needles (Schulz, *B.* 18, 2463).

Benzenyl-azoxim-benzenyl-*m*-carboxylic acid $C_6H_5.C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.C_6H_4.CO_2H$. [218°]. Formed by heating benzamidoxim *m*-carboxylic acid with BzCl (G. Müller, *B.* 19, 1497). White crystalline powder; sol. alcohol, insol. water.

Benzenyl-azoxim-butenyl $C_6H_5.C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.C_3H_7$. (265°). Oily fluid. Volatile with steam. Formed by the action of butyric anhydride upon benz-amidoxim, or by eliminating H_2O from the butyryl derivative of the latter (Schulz, *B.* 18, 1085).

Benzenyl-imidoxim-carbonyl $C_8H_6N_2O_2$ *i.e.* $C_6H_5.C\left\langle\begin{smallmatrix}N.O\\NH\end{smallmatrix}\right\rangle CO$ and $C_6H_5.C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C(OH)$. *Benzenyl-azoxim-carbinol.* [198°]. Carbonises at about 300°. Soluble in alcohol, ether, chloroform, benzene, and hot water, sparingly in cold water. The aqueous solution reacts strongly acid to litmus. It decomposes carbonates. Not attacked by PCl_5 or by HCl. Formed by elimination of alcohol from benzenyl-amidoxim-carbonic ether or, directly, by heating benzenyl-amidoxim with chloroformic ether.

Salts.—A′Ag: white pp.—A'_2Cu: green pp.

Ethyl derivative $C_8H_5EtN_2O_2$ [36°]; soluble in alcohol, ether, &c., nearly insoluble in water; indifferent body (Falck, *B.* 18, 2468; 19, 1481).

Benzenyl-azoxim-ethenyl $C_9H_8N_2O$ *i.e.* $C_6H_5.C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.CH_3$. [41°]. (244°). Formed by boiling benzenyl-amidoxim with acetic anhydride (Tiemann a. Krüger, *B.* 17, 1696; 18, 1059; Schulz, *B.* 18, 1084). Flat prisms. Easily volatile with steam. Sublimes at the ordinary temperature in white needles. V. sol. alcohol, ether, and benzene, sl. sol. water.

Benzenyl-azoxim-propenyl $C_6H_5.C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.C_2H_5$. (255°). Colourless oil. Volatile with steam. Formed by the action of propionic anhydride upon benz-amidoxim (Schulz, *B.* 18, 1085).

Benzenyl-azoxim-propenyl-ω-carboxylic acid $C_6H_5.C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.CH_2.CH_2.CO_2H$. [120°]. Formed by fusing benz-amidoxim with succinic anhydride. White trimetric plates or prisms. V. sol. alcohol, ether, hot water and benzene, insol. ligroïn. It is not decomposed by warming with H_2SO_4.

Salts. — A′Ag: white crystalline pp. — A'_2Ca $3\frac{1}{2}$aq: long glistening soluble needles.—A'_2Ba aq: short prisms, or monoclinic crystals. — A'_2Cu: bluish-green granular powder. — A′PbOH: granular pp.

Ethyl ether A′Et: (255°), yellowish oil.

Amide $C_{10}H_9ON_2.CONH_2$: [168°], slender needles (Schulz, *B.* 18, 2459).

***m*-Carboxy-benzenyl-azoxim-benzenyl** $C_6H_4(CO_2H).C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.C_6H_5$. [218°]. Formed by heating benzamidoxim-*m*-carboxylic acid with benzoyl chloride. White crystalline powder. Soluble in acetic acid, alcohol, and ether, insoluble in water and benzene. The aqueous solution of the ammonium salt gives pps. with $AgNO_3$ and $CuSO_4$ (Müller, *B.* 19, 1497).

***m*-Carboxy-benzenyl-azoxim-ethenyl** $C_6H_4(CO_2H).C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.CH_3$. [217°]. Formed by heating benzamidoxim-*m*-carboxylic acid with acetic anhydride. White crystalline powder. Sol. alcohol and ether, sl. sol. water and benzene. The aqueous solution of the ammonium salt gives pps. with $AgNO_3$, $CuSO_4$, $Pb(OAc)_2$, and $ZnSO_4$ (Müller, *B.* 19, 1496).

***p*-Carboxy-benzenyl-azoxim-ethenyl** $C_{10}H_8N_2O_3$ *i.e.* $C_6H_4(CO_2H).C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.CH_3$. [218°]. Formed by boiling benzamidoxim-*p*-carboxylic acid with acetic anhydride. Crystalline solid. Soluble in hot water and alcohol, more sparingly in ether and chloroform. The dilute solution of the ammonium salt gives pps. with $AgNO_3$, $Pb(OAc)_2$ and $CuSO_4$ (Müller, *B.* 19, 1492).

***m*-Carboxy-benzenyl-azoxim-propenyl-ω-carboxylic acid** $\overset{(3)}{C_6H_4}(\overset{(1)}{CO_2H}).C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.CH_2.CH_2.CO_2H$. [218°]. Formed by heating benzamidoxim-*m*-carboxylic acid with succinic anhydride. Needles. Sol. hot water, v. sol. alcohol and ether, sl. sol. chloroform, insol. benzene. The aqueous solution of the ammonium salt gives sparingly soluble pps. with $AgNO_3$, $CuSO_4$, and $Pb(OAc)_2$ (Müller, *B.* 19, 1496).

***p*-Carboxy-benzenyl-azoxim-propenyl-ω-carboxylic acid** $C_6H_4(\overset{(4)}{CO_2}\overset{(1)}{H}).C\left\langle\begin{smallmatrix}N.O\\N\end{smallmatrix}\right\rangle C.CH_2.CH_2.CO_2H$. Formed by heating benzamidoxim-*p*-carboxylic acid with an excess of succinic anhydride. Sol. alcohol, sl. sol. water, v. sl. sol. ether, insol. benzene and chloroform. Carbonises at a high temperature without melting. The dilute aqueous

solution of the ammonium salt gives insoluble pps. with $CuSO_4$ and $Pb(OAc)_2$, pps. soluble in hot water with $ZnSO_4$ and $AgNO_3$ (Müller, *B.* 19, 1498).

Ethenyl-azoxim-benzenyl

$CH_3.C\langle^{N.O}_{N}\rangle C.C_6H_5$. [57°]. Long white needles. Begins to sublime at 70°-80°. Easily volatile with steam. V. sol. alcohol, ether, and benzene, sl. sol. hot water, insol. cold water and ligroïn. Formed by heating ethenyl-amidoxim hydrochloride with benzoyl chloride (Nordmann, *B.* 17, 2754).

***m*-Nitro-benzenyl-azoxim-benzenyl**

$C_6H_4(NO_2).C\langle^{N.O}_{N}\rangle C.C_6H_5$. [160°]. Formed by the action of benzoyl chloride upon *m*-nitro-benz-amidoxim $C_6H_4(NO_2).C(NH_2)$:NOH (Schöpff, *B.* 18, 1067). White needles. Sublimable. Sol. alcohol, ether, and benzene, insol. water and ligroïn.

***m*-Nitro-benzenyl-azoxim-ethenyl**

$C_6H_4(NO_2).C\langle^{N.O}_{N}\rangle C.CH_3$. [109°]. White needles. Sublimable. Formed by the action of acetic anhydride upon *m*-nitro-benz-amidoxim $C_6H_4(NO_2).C(NH_2)$:NOH (Schöpff, *B.* 18, 1066).

***m*-Oxy-benzenyl-azoxim-benzenyl**

$C_6H_4(OH).C\langle^{N.O}_{N}\rangle C.C_6H_5$. [163°]. Formed by diazotising *m*-amido-benzenyl-azoxim-benzenyl and heating the aqueous solution. Yellow needles. Sublimable. Sol. alcohol, ether, and benzene, scarcely sol. water, insol. ligroïn.

Ethyl ether $C_{14}H_9ON_2(OEt)$: [71°]; fine felted crystals; soluble in alcohol (Schöpff, *B.* 18, 2475).

Phenyl-allenyl-azoxim-benzenyl

$C_6H_5.CH{:}CH.C\langle^{N.O}_{N}\rangle C.C_6H_5$. [102°]. *Cinnamenyl-azoxim-benzenyl.* Formed by elimination of H_2O from the benzoyl derivative of phenyl-acryl-amidoxim by heating it above its melting-point or by boiling it with water (Wolff, *B.* 19, 1509). Very slender white needles. V. sol. alcohol, ether, chloroform, and benzene, v. sl. sol. cold water. Sparingly volatile with steam.

Phenyl-allenyl-azoxim-ethenyl

$C_6H_5.CH{:}CH.C\langle^{N.O}_{N}\rangle C.CH_3$. [78°]. Sublimable. Colourless crystals. Formed by heating phenyl-acryl-amidoxim with acetic anhydride (Wolff, *B.* 19, 1509).

Phenyl - allenyl - azoxim - propenyl - ω - carboxylic acid

$C_6H_5.CH{:}CH.C\langle^{N.O}_{N}\rangle C.CH_2.CH_2.CO_2H$. [114°]. Formed by heating phenyl-acryl-amidoxim with succinic anhydride (Wolff, *B.* 19, 1511). Long white glistening prisms. Sol. alcohol, ether, benzene, and hot water, sl. sol. ligroïn.—A'Ag: white powder.

Phenyl-ethenyl-azoxim-benzenyl

$C_6H_5.CH_2.C\langle^{N.O}_{N}\rangle C.C_6H_5$. [82°]. Formed by boiling the benzoyl derivative of phenyl-acet-amidoxim with water for a long time (Knudsen, *B.* 18, 1070). White needles. Volatile with steam. V. sol. alcohol, ether, and benzene, insol. water.

Phenyl-ethenyl-azoxim-ethenyl

$C_6H_5.CH_2.C\langle^{N.O}_{N}\rangle C.CH_3$. (262°). Oil. Volatile with steam. Formed by boiling the acetyl derivative of phenyl-acet-amidoxim with water for a long time (Knudsen, *B.* 18, 1070).

Phenyl - ethenyl - azoxim - propenyl - ω - carboxylic acid

$C_6H_5.CH_2.C\langle^{N.O}_{N}\rangle C.CH_2.CH_2.CO_2H$. [60°]. Formed by fusing together phenyl-acet-amidoxim $C_6H_5.CH_2.C(NH_2)$:NOH and succinic anhydride. Prismatic plates. V. sol. alcohol and ether, sl. sol. cold, water, m. sol. hot. It is a strong acid.

Salts.—A'Ag: white pp.—A'_2Cu: bluish green pp. (Knudsen, *B.* 18, 2483).

Phenyl-oxy-ethenyl-azoxim-ethenyl

$C_6H_5.CH(OH).C\langle^{N.O}_{N}\rangle C.CH_3$. [65°]. Formed by heating the acetyl derivative of phenyl-oxy-acet-amidoxim $C_6H_5.CH(OH).C(NH_2)$:NOAc with water for some time. Transparent needles. Distils undecomposed, and is volatile with steam. V. sol. alcohol, ether, and benzene, sl. sol. cold water.

Acetyl derivative

$C_6H_5.CH(OAc).C\langle^{N.O}_{N}\rangle C.CH_3$. [52°]; fine white needles; volatile with steam; sol. alcohol, ether, and hot water, nearly insol. cold water (Gross, *B.* 18, 1076).

***p*-Toluenyl-azoxim-benzenyl** $C_{15}H_{12}N_2O$ *i.e.* $C_6H_4Me.C\langle^{N.O}_{N}\rangle C.C_6H_5$. [103°]. Formed by heating the benzoyl derivative of *p*-tolu-amidoxim, H_2O being split off (Schubart, *B.* 19, 1490). Long slender white needles. V. sol. ether, benzene, and chloroform, sl. sol. hot water, insol. cold.

AZOXINES.—Compounds whose molecular formulæ may be written $X''\langle^{NH}_{O}\rangle Y''$, such as

Phenazoxine $C_6H_4\langle^{NH}_{O}\rangle C_6H_4$ and

Naphthazoxine $C_{10}H_6\langle^{NH}_{O}\rangle C_{10}H_6$.

They may be formed:—(1) By heating aromatic imido-sulphides with copper oxide:

$$C_{10}H_6\langle^{NH}_{S}\rangle C_{10}H_6 + CuO = C_{10}H_6\langle^{NH}_{O}\rangle C_{10}H_6 + CuS;$$

(2) By heating *o*-amido-phenols with *o*-di-oxy-compounds: $C_6H_4\langle^{NH_2}_{OH} + {}^{OH}_{OH}\rangle C_6H_4 =$

$$C_6H_4\langle^{NH}_{O}\rangle C_6H_4 + 2H_2O$$

(Bernthsen, *B.* 20, 942).

AZOXY- COMPOUNDS, compounds whose molecular formula may be represented by

$$X{-}\overset{O}{\overbrace{N{-}N}}{-}X.$$

They are formed by treating nitro- compounds with alcoholic potash or sodium amalgam. They may be reduced to hydrazo- compounds, X—NH—NH—X, and finally to two molecules of an amine, X—NH_2. The products of nitration of azoxy- compounds are often unsymmetrical, $X{-}\overset{O}{\overbrace{N{-}N}}{-}Y$.

p-Aldehydo-benzoic azoxy-p-aldehydo-benzoic acid

$$C_6H_3\overset{(4)}{(CHO)}\overset{(1)}{(CO_2H)}.N\overset{(2)}{.}N.C_6H_3\overset{(4)}{(CHO)}\overset{(1)}{(CO_2H)}.$$
$$\diagdown O \diagup$$

Formed by reduction of nitro-*p*-aldehydo-benzoic acid with aqueous KCN. Colourless needles. V. sol. ether, alcohol, and chloroform, sl. sol. ligroïn, nearly insol. water. Decomposes at about 280°. It gives the ordinary reactions of an aldehyde.

Phenyl hydrazide: small golden yellow prisms (Homolka a. Löw, *B.* 19, 1090).

o-Amido-benzene-o-azoxy-aniline

Di-benzoyl derivative $(C_6H_4NHBz)_2N_2O$. [195°]. Prepared by acting on benzoyl-o-nitranilide dissolved in alcohol with zinc-dust and adding ammonia and platinic chloride. Bright yellow mass, insol. water, sl. sol. boiling alcohol (Mixter, *Am.* 6, 26).

m-Amido-benzene-m-azoxy-aniline [c. 272°].

Di-benzoyl derivative.—Prepared by dissolving *m*-nitro-benzanilide in boiling alcohol and adding alcoholic ammonia and powdered zinc together with a trace of platinum. Very light powder with pale yellow colour. Insol. alcohol, ether, and benzene (Mixter, *Am.* 5, 5).

p-Amido-benzene-p-azoxy-aniline $(C_6H_4NH_2)N_2O$. [182°-184°]. Prepared by the action of potassic ethylate on its diacetyl derivative. Sol. alcohol, giving a red solution. Sl. sol. boiling water, from which it separates on cooling as a fibrous yellow mass (Mixter, *Am.* 5, 4).

Di-acetyl derivative $(C_6H_4NHAc)_2N_2O$ [275°-278°]. Prepared by the action of powdered zinc and ammonia on *p*-nitro-acetanilide in alcoholic solution. Hair-like particles with light golden-yellow colour. Sl. sol. boiling alcohol.

Di-benzoyl derivative $(C_6H_4.NHBz)_2N_2O$. [310°]. Prepared by the action of zinc and ammonia on *p*-nitro-benzanilide. Light yellow colour. Insol. alcohol and water (Mixter, *Am.* 5, 284).

o-Amido-toluene-azoxy-o-toluidine [1:2:4] $C_6H_3Me(NH_2).N_2O.C_6H_3Me(NH_2)$ [4:1:2] *Azoxy-o-toluidine.* [168°]. From nitro-*o*-toluidine in alcoholic solution by sodium amalgam (Limpricht, *B.* 18, 1405; Graeff, *A.* 229, 344). Long orange silky needles (from alcohol), or yellow needles (from water). V. sol. alcohol, sl. sol. water. Converted by conc. H_2SO_4, by molecular change, into amido-toluene-azo-amido-cresol.

Salts.—$B''H_2SO_4\frac{1}{2}aq$: needles.—$B''2HCl$.—$B''H_2Cl_2PtCl_4$.—$B''2HBr$.

p-Amido-toluene-azoxy-p-toluidine [1:4:2] $C_6H_3Me(NH_2).N_2O.C_6H_3Me(NH_2)$ [2:1:4]. [148°]. Yellow needles. Sol. alcohol and hot water. Prepared by the action of sodium amalgam on an alcoholic solution of nitro-*p*-toluidine.—$B''(HCl)_2$: sl. sol. water.—$B''H_2Cl_2PtCl_4$ (Buckney, *B.* 11, 1451).

Benzoyl derivative $C_6H_3Me(NHBz).N_2O.C_6H_3Me(NHBz)$. [290°]. From $C_6H_3Me(NHBz)(NO_2)$ [1:4:2] by treatment with zinc and ammonia (Mixter, *Am.* 5, 285). Light yellow substance, insol. water and alcohol.

Benzene-p-azoxy-aniline $C_6H_4(NH_2).N_2O.C_6H_5$. [139°]. S. 4·27 at 21°. Formed, together with benzene-azo-aniline, by the action of ammonium sulphide on an alcoholic solution of benzene-azoxy-nitro-benzene (G. Schmidt, *A.* 122, 174; *Z.* [2] 5, 419). Large pale-yellow tables (from dilute alcohol). Sl. sol. hot water, v. sol. alcohol and ether. Reduced by tin and HCl to aniline and *p*-phenylene-diamine.

Salts.—B'HCl: silvery laminæ, saponified by water.—$B'_2H_2PtCl_6$.

Benzene-azoxy-benzene $C_6H_5.N_2O.C_6H_5$. Mol. w. 198. [36°]. S. (alcohol) 17·5 at 16°.

Formation.—1. From nitro-benzene by the action of alcoholic KOH (Zinin, *J. pr.* 36, 93; Rasenack, *B.* 5, 364; Schmidt a. Schultz, *A.* 207, 328; Wilsing, *A.* 215, 228), or sodium-amalgam (Alexejeff, *J.* 1864, 525; Moltchanoffsky, *J. R.* 1882, 350).—2. From aniline by oxidising with $KMnO_4$ (Glaser, *Z.* [2] 2, 308).—3. From benzene-azo-benzene by oxidising with CrO_3 (Petrieff, *B.* 6, 577).

Preparation.—1. By reducing nitro-benzene in alcoholic solution by means of sodium-amalgam. The yield is 87 p.c. of the theoretical (Moltchanoffsky, *J. R.* 1882, 224; *Bl.* [2] 38, 551).—2. By boiling nitro-benzene with sodium methylate, prepared from methyl alcohol (250g.) and sodium (10 g.), the reaction being as follows:

$$4PhNO_2 + 3CH_3ONa =$$
$$2Ph_2N_2O + 3HCO_2Na + 3H_2O$$

(Klinger, *B.* 15, 865).

Properties.—Pale yellow trimetric needles; insol. water, sol. alcohol, and ether. Small quantities may be volatilised with steam.

Reactions.—1. When mixed with neutral substances (*e.g.* NaCl) and *distilled* it gives aniline, azo-benzene, and other products.—2. *Ammonium sulphide* has hardly any action upon it in the cold, but on warming it reduces it to hydrazo-benzene.—3. $SnCl_2$ and HCl reduce it to aniline, very little benzidine being formed (Schmidt a. Schultz, *B.* 12, 484).—4. Warm conc. H_2SO_4 converts it into benzene-*p*-azo-phenol (Wallach a. Belli, *B.* 13, 525).—5. *Aniline hydrochloride* at 230° gives violaniline (v. Dechend a. Wichelhaus, *B.* 8, 1614).—6. *Diphenylamine hydrochloride* heated with it gives tri-phenyl-violaniline (Girard a. Caventou, *B.* 12, 290).—7. Conc. HBr at 250° gives di-bromo-aniline (Sendzink, *Z.* [2] 6, 266); HI gives benzidine.—8. PBr_5 gives yellow crystals of $C_{12}H_{11}N_2Br_3$ which are converted by aqueous $AgNO_3$ into benzene-azo-benzene (Werigo, *Z.* [2] 6, 387).—9. PCl_5 added to an ethereal solution gives benzene-azo-benzene (Werigo, *A.* 165, 202).—10. *Sodium amalgam* gives hydrazo-benzene.—11. *Sulphurous acid* forms benzidine sulphate.—12. *Nitric acid* forms three benzene-azoxy-nitro-benzenes (*q. v.*) and also a tri-nitro-derivative $C_{12}H_7(NO_2)_3N_2O$, [152°] (G. Schmidt, *Z.* [2] 5, 421). This is converted by CrO_3 mixed with conc. HNO_3 at 200° into $C_{12}H_7(NO_2)_3N_2O_2$, [102°], and $C_{12}H_7(NO_2)_3N_2O_3$, [52°] (Petrieff, *B.* 6, 558).

Benzene-azoxy-benzene-m-sulphonic acid $C_6H_5.N_2O.C_6H_4(SO_3H)$. [60°-70°]. Very deliquescent reddish-brown tables. Formed as a by-product in the oxidation of *m*-amido-benzene-sulphonic acid by $KMnO_4$.—KA' aq: long soluble tables (Limpricht, *B.* 18, 1420).

Benzene-azoxy-benzene-p-sulphonic acid $C_6H_5.N_2O.C_6H_4(SO_3H)$. [below 100°]. Red scales. V. sol. water. Formed as a by-product in the

oxidation of sulphanilic acid by $KMnO_4$; the yield is about 2 p.c.—$KA'2aq$: small yellow crystals (Limpricht, *B.* 18, 1420).

Benzene-azoxy-bromo-benzene sulphonic acid $C_6H_5.N_2O.C_6H_3Br(SO_3H)$. Formed as a by-product of the oxidation of bromo-amido-benzene-sulphonic acid $C_6H_3Br(NH_2)(SO_3H)$ [4:3:1] with $KMnO_4$.—$KA'2aq$: small red six-sided tables (Limpricht, *B.* 18, 1423). V. sol. water and alcohol.

Benzene-*p*-azoxy-nitro-benzene $C_6H_5.N_2O.C_6H_4NO_2$ [1:4]. [153°]. Formed together with the following body by the action of HNO_3 (S.G. 1·45) on benzene-azoxy-benzene (Zinin, *A.* 114, 218). Hair-like yellow needles. Reduced by alcoholic ammonium sulphide to benzene-*p*-azoxy-aniline.

Benzene-azoxy-nitro-benzene $C_6H_5.N_2O.C_6H_4.NO_2$. [49°]. Needles or prisms; prepared as above. Alcoholic ammonium sulphide forms a compound $C_{12}H_9N_3O(?)$ [85°].

Benzene-azoxy-nitro-benzene $C_6H_5.N_2O.C_6H_4(NO_2)$ [1:2]. [127°]. Formed by adding fuming HNO_3 (25–30 c.c.) to a solution of benzene-azo-benzene (20 g.) in glacial acetic acid (100 c.c.) at 75°. Red rhombic plates. Sol. alcohol, ether, and acetone. Alcoholic KOH gives an emerald-green colouration; by long boiling or by treatment with sodium-amalgam it is reduced to a compound $C_{24}H_{18}N_4O$ (Janovsky a. Erb, *B.* 20, 361).

Benzoic *o*-azoxy-benzoic acid [2:1] $C_6H_4(CO_2H)-N_2O-C_6H_4(CO_2H)$. [1:2]. Mol. w. 286. [237°–242°].

Formation.—1. By the action of KCN on *o*-nitro-benzaldehyde (Homolka, *B.* 17, 1902).—2. From *o*-nitro-benzoic acid by treatment with sodium-amalgam or alcoholic KOH (Griess, *B.* 7, 1611).—3. Together with *o*-nitro-toluene by boiling *o*-nitro-benzyl alcohol with aqueous KOH (Jaffé, *H.* 2, 57).

Properties.—Small colourless prisms; m. sol. hot alcohol, sl. sol. ether and boiling water. Reduced by sodium-amalgam to carboxy-benzene-azo-benzoic acid, and finally to hydrazo-benzoic acid.

Salt.—$BaA''4aq$.

Benzoic *m*-azoxy-benzoic acid [3:1] $C_6H_4(CO_2H).N_2O.C_6H_4(CO_2H)$ [1:3]. Formed by boiling *m*-nitro-benzoic acid with alcoholic KOH (Griess, *A.* 131, 92). Minute needles or plates. Insol. water, sl. sol. alcohol and ether. Reduced by tin and HCl to di-amido-diphenic acid.

Diazoxy-benzoic acid

$$C_7H_4N_2O_3 \text{ or } CO_2H.C_6H_3\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle O \left[1\,\begin{smallmatrix}3\\5\end{smallmatrix}\right] (?).$$

Formed by reducing di-nitro-benzoic acid dissolved in NaOHAq with sodium-amalgam (V. Meyer a. Michler, *B.* 6, 746; Michler, *B.* 7, 420; *A.* 175, 150). An amorphous black powder, insol. alcohol, ether, benzene, chloroform, and glacial acetic acid. Reduced by tin and HCl to diamido-benzoic acid. HNO_3 gives an amorphous nitro- derivative.

Salts.—AgA': black pp. sol. NH_3Aq.—BaA'_2: black pp.—ZnA'_2: brownish-black pp.

An isomeric acid, resembling the above, is formed from (1, 2, 4)-di-nitro-benzoic acid. It is not attacked by tin and HCl.

***m*-Bromo-benzene-*m*-azoxy-bromo-benzene** [3:1] $C_6H_4Br.N_2O.C_6H_4Br$ [1:3]. [112°]. From *m*-bromo-nitro-benzene and alcoholic KOH (Gabriel, *B.* 9, 1405). Bright yellow prisms; v. sl. sol. alcohol.

***p*-Bromo-benzene-*p*-azoxy-bromo-benzene** [4:1] $C_6H_4Br.N_2O.C_6H_4Br$ [1:4]. [172°] (Hofmann a. Geyger, *B.* 5, 919); [175°] (Werigo, *A.* 165, 198). From *p*-bromo-nitro-benzene by treatment with alcoholic KOH or sodium-amalgam. Yellow leaflets, v. sol. hot alcohol. Nitric acid forms a tri-nitro- derivative [174°].

Bromo-benzene-azoxy-bromo-benzene sulphonic acid $C_6H_4Br.N_2O.C_6H_3Br(SO_3H)$. Formed as a by-product of the oxidation of di-bromo-amido-benzene-sulphonic acid $C_6H_2Br_2(NH_2)(SO_3H)$ [1:3:6:4] by $KMnO_4$.—$KA'2aq$: very small yellow scales (Limpricht, *B.* 18, 1425).

***m*-Chloro-benzene-*m*-azoxy-chloro-benzene** [3:1] $C_6H_4Cl.N_2O.C_6H_4Cl$ [1:3]. [97°]. Formed by boiling *m*-chloro-nitro-benzene with alcoholic KOH (Laubenheimer a. Winther, *B.* 8, 1623). Yellowish-brown flat needles. V. sl. sol. alcohol. Treated with fuming H_2SO_4 it is chiefly converted into *m*-chloro-benzene-azo-chloro-phenol, only a very small quantity of *m*-chloro-benzene-azo-chloro-benzene being formed (Schultz, *B.* 17, 464).

***p*-Chloro-benzene-azoxy-chloro-benzene** [4:1] $C_6H_4Cl.N_2O.C_6H_4Cl$ [1:4]. [155°]. From *p*-chloro-nitro-benzene by treatment with alcoholic KOH (Heumann, *B.* 5, 910; *cf.* Willgerodt, *B.* 15, 1002), sodium-amalgam (Alexejeff, *Z.* 1866, 269), or (in ethereal solution) with sodium (Hofmann a. Geyger, *B.* 5, 916). Pale yellow needles, sl. sol. cold alcohol. Treated with fuming H_2SO_4 it is chiefly converted into *p*-chloro-benzene-azo-chloro-benzene only forming traces of a chlorinated benzene-azo-phenol (Schultz, *B.* 17, 464).

Di-chloro-benzene-azoxy-di-chloro-benzene [3:5:1] $C_6H_3Cl_2.N_2O.C_6H_3Cl_2$ [1:3:5]. [172°]. From (3,5,1)-di-chloro-nitro-benzene and alcoholic KHS (Beilstein a. Kurbatow, *A.* 197, 84).

Di-chloro-benzene-azoxy-di-chloro-benzene [2:5:1] $C_6H_3Cl_2.N_2O.C_6H_3Cl_2$ [1:2:5]. [112°]. From *p*-di-chloro-nitro-benzene and alcoholic KOH (Laubenheimer, *B.* 7, 1600; 8, 1623). Small bright yellow needles.

***p*-Chloro-benzene-azoxy-chloro-nitro-benzene** [4:1] $C_6H_4Cl.N_2O.C_6H_3Cl(NO_2)$ [1:4:?]. [184°]. From *p*-chloro-benzene-*p*-azoxy-chloro-benzene and HNO_3 (Heumann, *B.* 5, 912; 18, 1185). Bright yellow flocculent substance. V. sl. sol. boiling alcohol; reduced by alcoholic ammonium sulphide to *p*-chloro-benzene-azo-chloro-nitro-benzene.

Chloro-toluene-azoxy-chloro-toluene [6:3:1] $C_6H_3MeCl.N_2O.C_6H_3MeCl$ [1:6:3]. [128°]. Formed by the action of Na on an ethereal solution of chloro-nitro-toluene (Hofmann a. Geyger, *B.* 5, 919). Small needles.

***m*-Iodo-benzene-*m*-azoxy-iodo-benzene** [3:1] $C_6H_4I.N_2O.C_6H_4I$ [1:3]. From *m*-iodo-nitro-benzene and alcoholic KOH (Gabriel, *B.* 9, 1406). Flat yellow needles; sl. sol. cold alcohol.

***p*-Iodo-benzene-*p*-azoxy-iodo-benzene** [4:1] $C_6H_4I.N_2O.C_6H_4I$ [1:4]. [200°]. From *p*-iodo-nitro-benzene and alcoholic KOH (G.). Light yellow plates or scales. Sl. sol. hot alcohol.

Di-methyl-amido-benzene-azoxy-di-methyl-aniline [4:1] $C_6H_4NMe_2.N_2O.C_6H_4NMe_2$ [1:4]. From *p*-nitroso-di-methyl-aniline and alcoholic KOH (Schraube, *B.* 8, 619). Glittering brown crystals; sl. sol. water, m. sol. hot alcohol and benzene. The salts are decomposed by water.—$B''H_2PtCl_6$ aq.

***m*-Nitro-benzene-*m*-azoxy-nitro-benzene** [3:1] $C_6H_4(NO_2).N_2O.C_6H_4(NO_2)$. [1:3] [142°].

Preparation.—A solution of 2 or 3 pts. of *m*-di-nitrobenzene in about 15 pts. of methyl alcohol is mixed with a solution of sodium methylate prepared by dissolving 1 pt. of sodium in 20 pts. of methyl alcohol. A vigorous reaction sets in, which is completed by 48 hrs. cohobation; large yield. Long needles. V. sol. benzene, m. sol. ether and CS_2, v. sl. sol. cold alcohol. By heating to about 140° with strong H_2SO_4 it is converted into the isomeric di-nitro-oxy-azo-benzene $C_6H_4(NO_2).N_2.C_6H_2(NO_2)(OH)$ (Klinger a. Pitschke, *B.* 18, 2551).

***p*-Nitro-diphenyl-*p*-azoxy-nitro-diphenyl** $C_6H_4(NO_2).C_6H_4.N_2O.C_6H_4.C_6H_4NO_2$. [225°]. From *p*-di-nitro-diphenyl by acting on its alcoholic solution with sodium-amalgam (Wald, *B.* 10, 137). Brick-red crystalline powder; forms a red solution in conc. H_2SO_4. Insol. most solvents. Reduced by alcoholic ammonium sulphide to benzidine.

Nitro-oxy-benzene-azoxy-di-nitro-phenol

Diethyl ether

$C_6H_3(NO_2)(OEt).N_2O.C_6H_2(NO_2)_2OEt$. [168°]. From HNO_3 and the diethyl ether of *p*-oxy-benzene-*p*-azo-phenol: the product is exhausted with water, and then treated with alcohol. On cooling, the alcohol deposits the body in long yellow needles grouped in stars. Sol. ether, $CHCl_3$, C_6H_6 and glacial acetic acid (Andreae, *J. pr.* 129, 337).

An isomeric body. [187°]. This forms the greater part of the product of the nitration, and is left undissolved when the former body is extracted with alcohol. It is crystallised from acetic ether, in which it is very soluble.

***o*-Oxy-benzene-*o*-azoxy-phenol**

$C_6H_4(OH).N_2O.C_6H_4.OH$.

Ethyl ether $\{C_6H_4(OEt)\}_2N_2O$. *Azoxy-phenetol.* [102°]. By reducing a cold (0°) solution of *o*-nitro-phenetol (1 pt.) in alcohol (7 pts.) by adding sodium amalgam; on adding water a pp. is got; this is freed from azo-phenetol by washing with strong HCl as long as the latter is coloured (Schmitt a. Möhlau, *J. pr.* 126, 201).

Properties.—Colourless triclinic plates. In soluble in water, but melts in boiling water. Slightly soluble in cold alcohol, insoluble in hot alcohol. Not volatile with steam.

Diphenyl-azoxy-diphenyl

$C_6H_5.C_6H_4.N_2O.C_6H_4.C_6H_5$. [205°]. Small yellow plates. Insol. water and alcohol, sl. sol. acetic acid. Prepared by the action of alcoholic KOH on *p*-nitro-di-phenyl (Zimmermann, *B.* 13, 1961).

Phenyl-glycollic-*o*-azoxy-phenyl-glycollic acid $ON_2(C_6H_4O.CH_2.CO_2H)_2$. [187°].

Preparation.—*o*-Nitro-phenyl glycollic acid (18·6 g.), water (140 g.) and Na_2CO_3 (5 g.) are treated at 55° with sodium-amalgam (165 g. of 4 per cent. sodium), added in small portions. On cooling, crystals separate. These are dissolved in water and decomposed by HCl. The precipitated acids are recrystallised from alcohol. If the mixed acids now melt above 162°, they are etherified by alcohol and HCl. The ether of the azoxy- acid is less soluble in alcohol than that of the azo- acid, it is crystallised from alcohol and then saponified (A. Thate, *J. pr.* [2] 29, 152).

Properties.—Crystallises, from aqueous or dilute alcoholic solutions, with aq as short prisms or as scalenohedra; but if left in contact with the mother liquor these change to rhombohedra, taking up ½aq. Both these forms are sulphur-yellow. At 130° they become white and anhydrous. Dissolves in alkalis, HCl and glacial acetic acid. The solutions are yellow. Forms red solutions with HNO_3 and H_2SO_4. Insoluble in ether and in benzene.

Reactions.—1. *Lead acetate*, a yellowish-white flocculent pp.—2. $AgNO_3$ and $BaCl_2$, no pp. in hot solutions, on cooling a crystalline pp.

Salts.—$(NH_4)_2A''$: obtained, as a yellow micro-crystalline pp., by passing NH_3 into a solution of the acid in absolute alcohol. Its aqueous solution gives yellowish-white pps. with $BaCl_2$ and $Pb(OAc)_2$, yellow pps. with $AgNO_3$ and Fe_2Cl_6, and a green pp. with $CuSO_4$.—Ag_2A''.—$AgHA''$: more soluble than the neutral salt. BaA'' 2aq.

Ethyl ether.—Et_2A''; [114°]. White silky needles.

***m*-Sulpho-benzene-*m*-azoxy-benzene sulphonic acid** [3:1] $C_6H_4(HSO_3).N_2O.C_6H_4(HSO_3)$ [1:3]. [125°]. Prepared by the reduction of *m*-nitro-benzene-sulphonic acid with alcoholic KOH (Brunnemann, *B.* 11, 1048; *A.* 202, 240). Yellow needles. V. sol. water and spirit. $A''K_2$ 4aq: needles.—$A''(NH_4)_2$ 2½aq: rhombic pillars.—$A''Ba$ aq: difficultly soluble prisms. $A''Ca$ 3½aq: difficultly soluble needles.—$A''Pb$ aq.

Chloride [138°]. Yellowish-red pillars.

Amide [273°]: sl. sol. hot water.

Sulpho-naphthalene-azoxy-naphthalene sulphonic acid $C_{10}H_6(SO_3H).N_2O.C_{10}H_6.SO_3H$. From (α)-nitro-naphthalene-(α)-sulphonic acid and alcoholic KOH (Alen, *Bl.* [2] 45, 184). V. sol. water; conc. H_2SO_4 forms a violet solution.

Salts.—K_2A'' aq: trimetric tabular crystals. Na_2A'' 2aq: tables.—BaA'aq.—CaA' 2aq.—PbA' 2aq.

Terephthalic-azoxy-terephthalic acid

[6:3:1] $C_6H_3(CO_2H).N_2O.C_6H_3(CO_2H)_2$ [1:6:3]. Yellowish plates. Sol. hot, sl. sol. cold, water, v. sol. alcohol and ether. Decomposes between 250° and 280°. Obtained by oxidation of aldehydo-benzoic-azoxy-aldehydo-benzoic acid $N_2O(C_6H_3(CHO)CO_2H)_2$ with alkaline $KMnO_4$.

Salts.—$A^{iv}(NH_4)_4$: long yellowish prisms. $A^{iv}Ag_4$: yellow pp. (Honfolka a. Löw, *B.* 19, 1091).

Toluene-azoxy-bromo-toluene

$C_6H_4Me.N_2O.C_6H_3BrMe$. [74°]. From *p*-toluene-*p*-azoxy-toluene and bromine. Bright yellow tables; v. sol. alcohol and ether (Melms, *B.* 3, 551).

Toluene-azoxy-nitro-toluene

$C_6H_4Me.N_2O.C_6H_3(NO_2)Me$. [84°]. Formed by nitration of *p*-toluene-*p*-azoxy-toluene (Petrieff, *B.* 6, 557). Yellow needles.

Toluene-*o*-azoxy-toluene

$C_6H_4(CH_3).N_2O.C_6H_4(CH_3)$. [60°]. Formed by passing Cl_2O into an ethereal solution of *o*-hydrazo-toluene (Petrieff, *B.* 6, 557).

Preparation.—10 pts. of *o*-nitro-toluene are

added gradually to a solution of 5 pts. of sodium in 50 pts. by volume of methyl alcohol, the mixture being finally cohobated on the water-bath for 3 or 4 hours.

Properties.—Large yellow needles or plates; the crystals belong to the dimetric system, $a:b = \cdot 8416:1$.

Reactions.—By distillation with iron powder it yields *o*-azotoluene and a little toluidine. It also yields *o*-azotoluene by heating with H_2SO_4 (Klinger a. Pitschke, *B.* 18, 2553).

p-Toluene-*p*-azoxy-toluene $C_6H_4Me.N_2O.C_6H_4Me$. [70°] (M.); [59°] (P.). From *p*-nitro-toluene by reducing it in alcoholic solution with sodium amalgam (Melms, *B.* 3, 551; Petrieff, *Z.* [2] 5, 264; [2] 6, 30; *B.* 6, 557). V. sol. alcohol and ether.

Bromine gives a bromo- derivative, [74°], and a di-bromo- derivative [138°].

Nitric acid gives a nitro- derivative [84°], a di-nitro- derivative [145°], and a tri-nitro- derivative [201°].

AZOXYLENE *v.* *Xylene*-AZO-*xylene*.

AZOXY-NAPHTHALENE *v.* Naphthalene-AZOXY-naphthalene.

AZOXY-PHENOL *v.* Oxy-benzene-AZOXY-phenol.

AZOXY-DIPHENYL *v.* Diphenyl-AZOXY-diphenyl.

AZOXY-TOLUENE *v.* Toluene-AZOXY-toluene.

AZULENE or Azulin. Blue colouring matter present in essential oils of chamomile, wormwood, and millefolium. Causes these and other oils to give an absorption-spectrum, viz., three bands in red and orange (Hock, *Ar. Ph.* [3] 21, 17).

AZULMIC ACID $C_4H_5N_5O$. Flocculent brown pp. formed together with oxamide and oxamic acid by passing cyanogen into aqueous ammonia. Sl. sol. pure water, with violet fluorescence; acid or alkaline solutions fluoresce green. Boiling water slowly converts it into mycomelic acid $C_4H_4N_4O_2$. Nitric acid or $KMnO_4$ oxidises it to azulmoxin $C_4H_3N_5O_2$, an orange powder, insol. water, sol. conc. H_2SO_4, the solution having a deep-green fluorescence.

Hydrazulmin $C_4H_6N_6$ is formed by mixing dry cyanogen with dry NH_3. It forms black leaflets, converted by water at once into NH_3 and azulmic acid (Emmerling a. Jacobsen, *B.* 4, 927). By the spontaneous decomposition of an aqueous solution of HCN containing a little NH_3 a brown pp. is produced which, according to Gautier (*A. Ch.* [4] 17, 158), contains an azulmic acid of the formula $C_5H_5N_5O$.

AZURIN $C_{35}H_{32}N_4O_8$. [250·5°]. Small colourless tables forming solutions which have a splendid blue fluorescence. Prepared by heating salicylic aldehyde with *o*-tolylene-diamine (Ladenburg, *B.* 11, 596).

AZYLINES. Azo- compounds of the form $R_2N.C_6H_4.N:N.C_6H_4.NR_2$ prepared by passing nitric oxide into alcoholic solutions of tertiary aromatic amines; thus, di-methyl-aniline-azyline is described as di-methyl-amido-benzene-azo-di-methyl-aniline, di-amyl-aniline-azyline is described as di-amyl-amido-benzene-azo-di-amyl-aniline; and di-ethyl-aniline-azyline as di-ethyl-amido-benzene-azo-di-ethyl-aniline (Lippmann a. Fleissner, *M.* 3, 705; 4, 284, 788; *B.* 15, 2136; 16, 1421; Nölting, *B.* 18, 1143).

B

BABLAH. The fruit of several species of *Acacia*. The seeds and husks are rich in tannin.

BACCARINE. An alkaloid in *Baccharis cordifolia* or 'Mio-Mio.' Needles, sl. sol. water, sol. alcohol, amyl alcohol, and ether. Its aqueous solution is neutral to litmus (Arata, *Ph.* [3] 10, 6).

BACTERIA.—The name given originally to a common rod-like form which is assumed in the course of growth by the minute plants to which Nägeli (6) in 1857 applied the term Schizomycetes: hence the term 'Bacteria' is very frequently used to designate the whole of this group of organisms.

The Bacteria, Bacteriaceæ, or Schizomycetes are a group of plants of extreme simplicity of structure and very minute in size. Like larger fungi, they are destitute of chlorophyll, and accordingly are unable to decompose carbonic acid in the presence of sunlight; as a consequence their nutrition resembles in some respects that of animals, since they are dependent on the complex chemical substances produced by other organisms. The variety of substances containing either C or N, or both, which they can attack and make contributory to their sustenance is very great, whilst the chemical changes which they bring about in these substances are no less varied and remarkable. The exact nature of these changes and the relation of the Bacteria themselves to the substances upon which they feed form an enormous field of inquiry which has only recently been looked at by chemists, and that, as yet, very cursorily. The study of the forms presented by different kinds of Bacteria in the course of their growth is also as yet in an incomplete state, and whilst it is certain that there are kinds of Bacteria characterised each by its particular forms, its particular pabulum or chemical food, and by its particular chemical operations resulting in the formation of definite chemical products from the breaking up of the appropriate pabulum, we do not yet know in any large number of cases whether a particular form is constantly associated with particular chemical conditions and results, or whether it is possible under modified conditions for a given form to change its chemical and physiological activities. In a certain number of cases we *do* know that modified chemical and physical conditions will cause a given form in the course of its growth to acquire a very marked modification of form. Hence it is at present im-

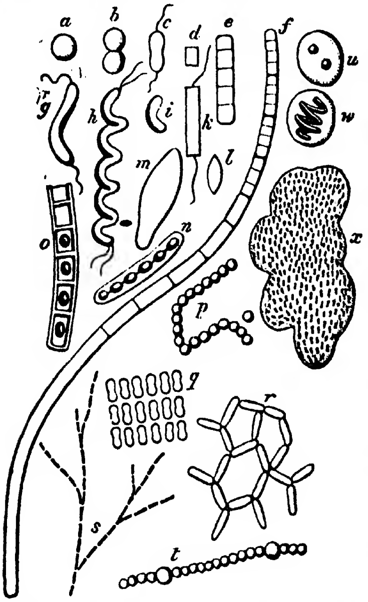
possible to discriminate with assurance different 'species' of Bacteria, although botanists use particular names to designate those which, so far as our information yet goes, are characterised by the constancy of a certain range of form, or in addition to this, by the constancy of chemical and physiological activity. By 'species' the naturalist understands a group of organic forms the members of which may present very little or very great differences of form and even of activities as compared one with another, but of which it is true, either that they actually are connected with one another by natural processes of reproduction which have occurred within human experience and observation, or that there is good reason to suppose that they might be so connected within human experience. Forms which are separated from one another by an interval the passage of which has not been witnessed and recorded by observers in the past, or defies experiment at the present day, are distinct species. We have not by experimental breeding produced a horse from an ass or an ass from a horse, or both from a third form, and we have no record of observations leading to the inference that such a passage has occurred *within human experience*, hence the horse and the ass are distinct species. On the other hand, we have traditional and experimental evidence of the production of the varieties of fancy pigeons from the Rock Pigeon, and conversely we know that from the most fantastic of fancy pigeons the Rock Pigeon can be produced in the course of a few generations: hence the Rock Pigeon and the Tumbler, Pouter, Fantail, Carrier, &c., are all variously modified members of one species.

It is necessary to allude to the question of species here because the progress of our knowledge of Bacteria in the immediate past has consisted in an important degree in the recognition of the fact that a great variety of microscopic forms may belong to one and the same species of Bacterium, and because we have to expect the most important advances in the future from the endeavours of bacteriologists experimentally to breed by change of conditions one kind of Bacterium from another, and even to create experimentally new kinds; and this in spite of the fact that it has been unjustifiably assumed that the forms of Bacteria at present recognised are of the nature of species and immutable.

Classificatory position of Bacteria.—The nearest allies of the Bacteria among chlorophyll-bearing plants are the Oscillatoriæ and certain green-coloured organisms (the so-called B. chlorinum, B. virens, B. viride) which, whilst identical in form with some of the Bacteria, differ physiologically from them in possessing chlorophyll. The distinction between these plants and the Bacteria is not by any means a wide one, and there can be no doubt of the close genetic relationship of the green and the greenless Schizophyta, the Bacteria having, as is the case in other groups of plants, lost their chlorophyll and acquired parasitic or saprophytic (refuse-eating) habits *pari passu*.

Forms of Bacteria.—The Bacteria present themselves either as swarming accumulations of detached cells or as linear aggregates (filaments or chains) of cells. Frequently the cells or plastids are loosely packed side by side and embedded in a jelly so as to form sheets or massive aggregations. The individual cells are usually extremely minute, being only ·001 mm. or even less in diameter, though they may be larger. The cells consist of a homogeneous protoplasm in which no nucleus can be detected; a cell wall, sometimes extremely delicate, bounds the surface of the cell, consisting of 'mycoprotoin,' rarely of cellulose. When the cell-wall swells up, imbibing water, a jelly is formed in which the cells are set at intervals ('zooglœa' condition). The ultimate shape of the cells of the Bacteria varies: it may be spherical (coccus-form or micrococcus), biscuit-shaped or keyhole-shaped, like two spheres partially fused (clithridium-form or bacterium *sensu stricto*), cuboid, varying from a cube to a short prism (micro-bacillus form), rod-shaped (bacillus-form), curved like a bent rod (comma-form), twisted like a fraction of a corkscrew (spirillum-form; if the spiral is not strongly marked, vibrio-form). The most characteristic feature of these cells is their power of rapid growth and multiplication by fission into two equal portions. Brefold has observed a Bacterium, formed by fission, grow to the size of the parent cell and itself divide into two in the course of half an hour, each of the daughter cells repeating the process in half an hour. In the course of 24 hours there are thus produced from a single Bacterium more than a billion individuals like itself. The constant and rapid process of binary fission is what has led to the use of the names Schizophyta and Schizomycetes. All the forms of cells which we have enumerated as being assumed by Bacteria exhibit this phenomenon. But it is not necessary that the results of the fission should separate entirely from one another. Frequently such separation occurs, and in the forms known as *clithridium* (or bacterium *sensu stricto*) *bacillus, vibrio, and spirillum*, a filament of naked protoplasm is frequently observed hanging from each end of the fission-product, and by its lashing movements causes an active 'swarming' movement, or darting progression of the separate cells. Contrasted with this locomotive swarming phase we have to note the phase of aggregation or continuous growth. As the result of variation in their pabulum, Bacteria which were at one hour separating from one another after fission—may remain in the next hour of growth in contact—held by their unruptured cell-walls. Thus are produced, in place of motile swarming individual cells, aggregates or colonies which may be (1) linear; (2) tessellate; (3) branched; (4) retiform; (5) massive. Any of these forms of aggregation may be exhibited by any of the different forms of cells. Linear aggregates of micrococci are called rosary-chains or streptococcus; linear aggregates of micro-bacilli form longer bacilli and so-called leptothrix filaments; linear aggregates of comma-shaped segments form spirilla; and small spirilla and vibrios when aggregated end to end form larger spirilla. Branched aggregation is seen in the so-called *Cladothrix dichotoma*, where a leptothrix filament breaks so as to allow a new line of growth to start at the broken surface, but without separation of the original continuation of the filament which takes up a lateral position as a 'false'

branch (fig. s). Similarly mesh-works (resembling those of the green hydrodictyon) are produced (fig. r), and very regular tessellate aggregates (fig. q). In the latter, bacillus or clithridium forms may be arranged with absolute symmetry forming little plates of twenty or more cells, in rows of five or more (merismopedia form). In the sarcina form the grouping is cuboid, 'packets' being produced instead of



FORMS OF BACTERIA. *a.* Micrococcus; *b.* Diplococcus; *c.* Clithridium or biscuit (with flagella); *d.* Microbacillus; *e.* Bacillus (built up of microbacilli); *f.* Leptothrix or filamentous form, homogeneous at one end, divided into bacilli in the middle and into microbacilli at the other end; *g.* Spirillum (vibrio); *h.* Spirillum (close spiral) with flagella; *i.* Comma (segment of spirillum); *k.* Homogeneous bacillus with flagella; *l.* Ovoid or double-cone form; *m.* Large irregular form: these may occur of great size and various shapes, as flat discs (macroplasts) in Bact. rubescens.—*Lank.*; *n.* Bacillus with moniliform protoplasm, *not* spores (B. tuberculosis); *o.* Sporobacillus, with endospores; *p.* Rosary-chain; linear aggregate of micrococci; *q.* Merismopedia-form or tablet; tesselate aggregate of clithridia; *r.* Hydrodictyon-form: retiform aggregate of bacilli; *s.* Cladothrix-form: false-branching linear aggregate of bacilli; *t.* Nostocoid linear aggregate; larger cocci occur at intervals in a chain of smaller cocci (observed in cultivations of B. anthracis); *u.* Two micrococci embedded in jelly-like envelope; *w.* Leuconostoc-form: a spirillum with jelly-like envelope; *x.* Zoogloea of clithridia: clithridia embedded in jelly-like matrix.

'plates.' Lastly, where the cell-wall swells up and forms a jelly, we may have the bacterian cells of any one shape adhering by the jelly to one another (fig. x), and forming spherical or irregular masses of jelly (zoogloea). These masses often are as large as the hand of a man, and are found on putrefying liquids and solids.

There is no doubt that all the forms of cell and of cell-aggregates which have been above described, and others to boot, may be exhibited by one and the same species of Bacterium. The *Bacterium rubescens* of Lankester [1] forms port-wine coloured pellicles on decaying organic matter in fresh-water ponds and in salt-marshes, the protoplasm of the cells being coloured by a peculiar insoluble pigment 'bacterio-purpurin.' Lankester found all the varieties of aggregation and of cell-form (except spirilla, since observed by Warming [2] and by Giard [3]), in a small tank in which this organism was flourishing; their connection with one another was proved by their all containing the peculiar colouring matter and by transition-forms of growth. The accuracy of these observations has been confirmed by Zopf [4], and Lankester's conclusions adopted by him as well as by De Bary [5]. The species of Bacteria are said to be 'pleomorphic' or in Lankester's phraseology 'protean.' Nevertheless it is exceedingly probable that not all bacterian species exhibit so wide a range of form as does B. rubescens. Some seem to be limited to the micrococcus and clithridium cell-forms, and to exist either as free swarming cells of those shapes, or as linear aggregates of the same. Others again are possibly limited to the micrococcus form, though it is necessarily extremely difficult to be sure that under appropriate conditions of cultivation the cell-form and aggregation-form will not change altogether, and, until experiments have been very carefully made in each case with the object of breaking down the limitation of form usual to this or that species of Bacterium, it will not be justifiable to dogmatically characterise a species of Bacterium by reference to its shape.

Spore-formation.—The Bacteria reproduce with enormous rapidity by fission, but some few are known to produce special reproductive bodies which have the property of resisting the injurious effects of desiccation and heat.

In one sense of the word 'spore,' every segment into which a previously unbroken plastid or cell of a Bacterium divides is a spore. A more special justification of the use of the term is found when occasionally one of the products of division is larger or more refringent than its fellows. Such 'spores' are recognised in the cultivations of Bacterium (Bacillus) tuberculosis. None of these are sufficiently specialised as reproductive particles to justify thoroughly the use of the term 'spore' in regard to them. In certain species, however, *e.g.* Bacterium subtile, Bacterium anthracis, and B. megaterium—the formation of well-defined endospores is characteristic. The protoplasm within each member of a linear aggregate of bacillus-forms separates centrally from itself an ovoid mass (fig. o), on the surface of which a coat of dense mycoprotein is produced. The bacilli themselves die away and decompose, but the ovoid spores remain, and have the power when dried of resisting an exposure to boiling water for as much as fifteen minutes. This property in the spores of B. subtile, which are common in old hay, has led to erroneous inferences as to the 'spontaneous generation,' or 'abiogenesis,' of Bacteria. It is possible, as suggested by De Bary [5], that the Bacteria which produce endospores are widely separate (as to their origin from green algae) from the other Bacteria which have no special-

ised spores. He divides the Bacteria into Endosporea and Arthrosporea.

Classification and nomenclature of Bacteria. For the present De Bary's division of the Bacteria into Endosporea and Arthrosporea may be accepted. The various generic names in use, such as Streptococcus, Ascococcus, Cladothrix, Beggiatoa, Myconostoc, Leuconostoc, have no logical basis, and produce a good deal of confusion by a false appearance of order. It is probably sufficient at present to limit generic distinctions to the three terms Micrococcus, Bacterium, and Sporobacterium. The genus Micrococcus comprises those Bacteriaceæ which are not at present known to exhibit any form of plastid or cell other than that of minute spheres; the genus Bacterium contains only those Bacteriaceæ which are known to exhibit in the course of growth rod-like forms of plastids, as well as in many cases micrococcus-forms and spiral and straight filamentous forms; the genus Sporobacterium includes only those forms which produce endospores, the so-called Bacterium (Bacillus) anthracis, B. subtile, and B. megaterium. Adhering to this nomenclature, we still make use of the terms vibrio, spirillum, bacillus, clithridium, ascococcus, zooglœa, &c., &c., to describe conditions of growth or varieties of cell-form.

With regard to the use of specific names, it is well that every form or group of forms of Bacteriaceæ which definitely recurs in certain conditions, and seems to be, so far as observation has gone, distinct from other known forms or groups of forms, should receive a name. Seeing that many of these names are probably but of temporary significance, it would be well that they should be as definitely descriptive of some feature of the supposed species as possible. The Bacteriaceæ should be named according to their chief properties, place of occurrence, or character of growth, and not after persons.

The following is a list of some of the chief supposed species of Bacteriaceæ which have been described, with an indication of the mode of occurrence. It is by no means an exhaustive list, and it is quite certain that some of the few supposed species here enumerated will, on further inquiry, be found to be phases of growth of other species.

Section A.: *Endosporea.*

Genus Sporobacterium.

Species: *S. subtile*, common in hay; *S. anthracis*, in the blood of cattle, sheep, and man, causes the disease known as splenic fever; *S. megaterium*, observed on boiled cabbage; *S. butyricum*, the butyric ferment, occurs in cheese-making, and has been confused with *S. subtile*.

Section B.: *Arthrosporea.*

Genus Bacterium.

Species: *B. termo*, the commonest form in putrefying vegetable infusions, but not yet isolated and characterised; *B. lineola*, a larger form occurring in foul ponds and sewage; *B. rubescens*, the protoplasm is wine-red in colour, the plastids and aggregates are of the most varied forms, occurs in ponds on vegetable refuse; *B. dichotoma*, forming branched aggregates (cladothrix) and straight and spiral filaments, common in river water on dead leaves; *B. Kuhniana*, in wells and drain-pipes (Crenothrix); *B. mesenteroides*, forming masses like frog-spawn on the beet-root juice of sugar refineries; *B. tuberculosis* (fig. n), in the diseased growths of men and animals suffering from tubercular consumption or phthisis; *B. lepræ*, in the diseased skin of persons suffering from leprosy; *B. mallei*, in men and horses affected with glanders; *B. typhosum*, in the spleen and intestinal glands in fatal cases of typhoid fever; *B. acidi lactici*, in sour milk, the manufacturer of lactic acid; *B. cyanogenum*, in milk, causing it to turn deep blue; *B. pyocyaneum*, in pus in badly dressed wounds, producing an emerald-green colouring matter; *B. alvei*, causing a disease in bee-larvæ known as foul-brood; *B. ureæ*, in urinals, causing the ammoniacal fermentation of urea; *B. aceti*, the vinegar ferment, causing the conversion of ethylic alcohol into acetic acid, occurs in vinegar factories; *B. prodigiosum*, causing blood-red staining of bread, milk, &c., leading to public alarm, and regarded as a portent; *B. ovatum*, causing the silk-worm disease known as 'pebrine;' *B. cuniculicidum*, causing a specific septicæmia in mice and birds: *B. choleræ gallinarum*, in the blood and in the intestines of fowls suffering from chicken cholera; *B. pneumoniæ crouposæ*, in the exudation in croupous pneumonia of man; *B. Kochii*, Koch's comma-bacillus, found in the intestines of persons dead of Asiatic cholera (this is a spirillum form which breaks into comma-shaped segments; it is not proved to have any causal relation to cholera); *B. Finkleri*, similar to the last but larger, occurs in ordinary diarrhœa; *B. buccale* and *B. Lewisii*, spiral and filamentous forms breaking into commas which occur in the healthy human mouth.

Genus Micrococcus.

Species: *M. pyogenes*, in acute abscesses; *M. erysipelatosus*, the cause of erysipelas in man; *M. variolæ*, in the pustules of small-pox; *M. gonorrhœæ*, probably the cause of gonorrhœa; *M. bombycis*, causing the disease in silk-worms known as flaccidezza; *M. ventriculi*, in the human stomach, observed in vomit, the 'sarcina ventriculi' of Goodsir; *M. scarlatinæ*, probably the cause of scarlet fever in man, and of a disease of the udder in cows; *M. rabidorum*, the cause of rabies, not satisfactorily isolated as yet; besides a list of twenty or thirty more causing special kinds of pyæmia in such animals as rabbits and mice, or producing well-marked colouring matters in colourless vegetable or animal infusions, green, blue, red, yellow, purple.

For a complete enumeration of the supposed 'species' of Bacteriaceæ which have been described, together with a description of each species and many illustrative figures, the reader is referred to the extremely useful and trustworthy treatise by Dr. Edgar Crookshank, entitled *A Manual of Bacteriology*, published by H. K. Lewis, London, 1887. Dr. Crookshank gives complete references to the original description of every known species and to the subsequent literature.

Chemical relations of the Bacteriaceæ.—The above incomplete list gives some idea of the importance attaching to these minute organisms. It is an importance entirely depending on the variety and peculiarity of the chemical decompositions and reconstructions which they excite in the organic compounds forming either the

living or dead bodies of higher plants and animals. Without Bacteria there would be no such thing as putrefaction, and therefore no circulation of the organic elements from their more stable compounds to the condition of albumens, fats, and sugars, and back again to the stable results of putrescence. The earth's surface would be cumbered with the dead bodies of former generations in which the carbon and nitrogen now serving as the food of plants would be permanently locked up. All the evil smells which are not directly due to the chemist, are, with few exceptions, due to the action of Bacteria. Many valuable commercial products, such as acetic acid, lactic acid, and flavouring compounds such as butyric acid, are obtained through their agency. The pungent fumes of stable refuse are caused by their action on urea. It is almost certain that they too are the agents of nitrification in the soil—one species of Bacterium (or Micrococcus?) converting the ammonia produced by another, into nitrates and nitrites. Some Bacteria produce highly poisonous bodies by their action on the albumens of dead animals and plants; amongst these poisons are the ptomaïnes, which have recently excited the attention of chemists [6]. Other Bacteria make their way into living animals and plants and there produce poisonous decomposition-products from the albuminous constituents of the organism, which are recognised in their effects under such names as splenic fever, scarlet fever, phthisis, rabies, &c. It appears that there are many kinds of Bacteria which are parasitic in and on the bodies of men and of other animals, the results of whose chemical activity is not injurious, whilst other kinds (or possibly the same kinds under changed conditions) produce deadly results. Other kinds again, it now seems certain, are not merely innocuous but actually necessary to the healthy life of the animal they inhabit. The digestion of food in the alimentary canal of man and other animals is largely aided by the Bacteria which are present in the intestine in countless myriads, and it appears that the products of digestion owe their chemical characteristics in no small degree to the Bacteria. In the absence of the normal parasitic Bacteria the products of digestion in the human intestine would, it appears highly probable, be of such a nature as to act poisonously when absorbed into the blood. When to these considerations we add the fact that the Bacteria are ubiquitous, abounding in the dust of the air, in all natural waters, and upon all surfaces whether of animate or inanimate objects which have not been chemically cleansed within a few seconds of their examination, some idea may be formed of the immense importance which belongs to the study of the Bacteria in the immediate future.

Methods of Study.—At present the state of knowledge of the chemical relations of the Bacteria is extremely fragmentary. They were originally discovered by Leeuwenhoek [7], the Dutch naturalist, in the fluids of the mouth, and various forms were subsequently seen with the microscope in natural waters, ponds, &c., and described by Ehrenberg [8] and others. It was Theodore Schwann [9], however, who, in 1838, demonstrated by a simple experiment that the Bacteria cause the putrefaction of organic substances, and that without them there is no putrefaction. Later, Pasteur [10], in opposition to Liebig, extended Schwann's observations and conclusions, and established the doctrine of organised ferments, which has proved of immense practical importance, and is as yet only at the commencement of its history. The foundation of the experimental demonstrations of Schwann and of Pasteur lies in the fact that the living protoplasm of the Bacteria is destroyed—that is to say, undergoes an irrevocable chemical change—when subjected to a temperature below or about that of boiling water. Consequently it is possible, by the action of heat, to destroy the Bacteria present in an experimental vessel and its contents, and to protect the contents from the further accession of Bacteria. By this method, and by this method alone, it has been possible to prepare organic infusions, as well as solid gelatine, albumen, &c., which, whilst capable of supporting the life of Bacteria, are yet free from their presence for the time being. Such substances are said to be 'sterilised.' They can be inoculated at pleasure with Bacteria and the effects of the inoculation studied. In order to procure the Bacteria for inoculation in a state of purity, special methods have been devised. So abundant and varied are the kinds of Bacteria present in nearly all natural organic material, that any rough process of inoculation will introduce many kinds of Bacteria simultaneously into a sterilised medium. To separate the various kinds of Bacteria for the purpose of study of each in its isolated condition, three principal methods are employed. The first applies, as at present is known, to but one kind, the *Sporobacterium* (*Bacillus*) *subtile*. The dry spores of this Bacterium resist the destructive effect of boiling water for as much as fifteen minutes, whilst all other known Bacteria are destroyed by it. Hence we have only to boil old hay in water for a few minutes in order to obtain a pure cultivation of B. subtile. The second method (due to Nägeli [11]) is that of fractional dilution. Given a liquid swarming with a mixture of various Bacteria, of which it is estimated by inspection that one individual in twenty is of the kind it is desired to cultivate. Dilute the liquid to such an extent that one drop of it should contain but a single bacterium. Then it is probable that every twentieth drop will contain a single isolated individual of the desired Bacterium. Fifty tubes of sterilised nutrient material are prepared, and into each a single drop of the diluted Bacterium-holding fluid is introduced. One, or possibly more, of the tubes will thus be inoculated with an isolated example of the desired Bacterium, which will multiply in the sterilised nutrient material and thus yield a pure cultivation, and can be recognised by the microscope. The third method is due to Brefeld, of Berlin. By streaking with a needle point a minute drop of fluid containing various Bacteria, over a surface of solid sterilised gelatine, the various Bacteria will be locally isolated along the course of the streak. They will remain thus separated from one another and commence to multiply *in situ*. With a low power of the microscope and a fine needle samples can be now removed from the various

patches of growth and placed in the pure condition in tubes of sterilised nutrient material for further cultivation and study. Similar isolation is effected by mixing liquid gelatine with a dilute infected liquid; when the gelatine solidifies, the various bacteria are embedded apart from one another, and grow in isolated patches, which can then be removed and separately studied by further cultivation.

Conditions of life required by Bacteria.—*General results.* (a).

1. The first general result of these methods of study has been to determine the ubiquity of a large number of different kinds of Bacteria, and the comparative rarity of others. More will be said below as to the study of the distribution of Bacteria in air and water.

2. The Bacteria are found to differ from one another in their relation to free oxygen; the aërobic (Pasteur) will only multiply in the presence of free oxygen; the anaërobic will not flourish except in the absence of free oxygen, or at any rate are indifferent to its presence. Thus B. anthracis is eminently aërobic, whilst the Bacterium of malignant œdema is anaërobic. The hay-bacillus (B. subtile) is aërobic, the butyric bacillus of cheese (very similar to the former in appearance) is anaërobic.

3. The source of nitrogen required by Bacteria for building up their protoplasm is various. Very many can take it in as low a form of combination as ammonia. Others require it in higher combination, and some either *require* it in the form of albumen or at any rate *can* take it from albumens. It is from albumens that some of the most remarkable products formed by Bacteria result. Th[illegible] be little doubt that the first steps in this process are comparable to the digestion of albumen by animal cells. It is not ascertained that all and any Bacteria can attack albumens. The exact range of the chemical quality of the nitrogenous food possible to each species of Bacterium has yet to be determined.

4. The carbon required by Bacteria may be taken in as low a form as acetic acid by certain species; others can take it from tartaric acid; others can do with nothing lower than a sugar; others again require glycerin or a similar body, and others apparently require their carbon as well as their nitrogen to be presented in the form of a proteid. Thus it results that many Bacteria can be nourished by solutions of ammonium tartrate alone, whilst the limits of complexity of necessary food-compounds has various ranges in other species, all of which require accurate determination by the chemist. Little has as yet been ascertained in this direction, but recently Dr. Roux [12] of the Pasteur Institute, has made an extremely important observation showing the necessity for extended research of the kind. It was found by Koch extremely difficult to cultivate the Bacterium tuberculosis, even upon blood-serum kept at the normal temperature of the body. Roux found that the addition of a minute quantity of glycerin to the serum led to the rapid and abundant growth of the B. tuberculosis supplied with that mixture; and further, that an ordinary meat broth which alone cannot serve as pabulum for the B. tuberculosis, when mixed with a minute quantity of glycerin acts as a most efficient nutrient medium for this species. It is highly probable that other such special requirements in regard to the chemical nature of their food, exist in respect of other species of Bacteria, whilst others again are more catholic in their nutrition.

5. Water is necessary for the growth of Bacteria as of all living things. Most Bacteria will flourish in the presence of that small amount of water in proportion to solid matter which suffices to constitute mere dampness or moistness. Bacteria are not killed by partial desiccation, but none resist thorough desiccation. In this respect important variations have been determined in different kinds. The spores of the Endosporea have a special power of resisting desiccation.

6. There is an optimum temperature favouring the growth of Bacteria, which ranges in various species from 10° to blood heat. Experiments have been made proving that certain species of Bacteria are killed by extreme cold, whilst all are arrested in growth during exposure to the freezing temperature of water. The most careful observations have been made in regard to the effects of exposure to high temperature. Exposure to a temperature of 100° for five minutes kills all Bacteria except those belonging to the Endosporea, the spores of which can resist the effects of this exposure for half-an-hour, and possibly longer. Many Bacteria are killed at lower temperatures (*e.g.* 80°), but careful experiments are wanting.

7. Experiments as to the effects of diminution and increase of atmospheric pressure upon the life of Bacteria have been made, but without reference to particular species. Diminution of pressure is not known to have any influence, whilst experiments made by the writer show that a pressure of thirty atmospheres does not hinder the development of putrefactive Bacteria appreciably, though modifying the chemical results of their life-processes. Extremely high pressures are stated to be destructive of Bacteria.

8. The influence of light is, according to the experiments of Downes [13], inhibitory to the growth of certain Bacteria, but the species so affected have not been determined. This is in accordance with the absence of protective pigment in most species, and the general fact of their growth within turbid liquids and beneath the surface of solid bodies away from the light.

9. Like the yeast-plant, which creates a poison (alcohol) in the nutrient fluids in which it grows, which after reaching a certain percentage causes the arrest of growth and the subsidence of the yeast-cells—so the Bacteria are limited in their growth by the existence of products of their own formation. These products have not been investigated by chemists. But it appears to be established that putrefactive Bacteria growing in a nutrient medium flourish for a time abundantly, then suddenly cease their growth and sink to the bottom of the vessel in which they have been growing, *although the nourishing material is not exhausted.* A further and exact investigation of this phenomenon by the chemist in regard to various species of Bacteria must lead to results of the

greatest value in relation to the practice of preventive inoculation for disease.

10. A condition of the life of a given species of Bacterium is found in the presence of other species of Bacteria. Frequently one species of Bacterium is the indispensable friend and associate of a second—preparing by its chemical activity the pabulum on which alone the second can thrive. An association of the kind is seen in what is called the vinegar plant, where Mycoderma prepares from starch the alcohol which the Bacterium aceti converts into acetic acid. So, too, the Bacterium of ammoniacal fermentation is the antecedent of the Bacterium which converts ammonia into nitrites and nitrates. Equally important is the inhibition and possibly the destruction of one species of Bacterium by another. Very little has been ascertained on this important matter, but it appears that the presence of certain putrefactive Bacteria in a nourishing medium will actually prevent the development and growth of certain pathogenic species of Bacteria, although these are present in small numbers. Apart from the question of possible specific incompatibility of two Bacteria, it appears that the question of quantity (*v.* Cheyne [14]) is important. A species of Bacterium which is at the commencement of an inoculation experiment one hundred times more numerous than a second species, may by its rapid development and numbers prevent altogether the growth of the second species.

11. The question of the conditions of life of the Bacteria involves the very important one of their tolerance of the presence of various chemical substances in the liquids in which they grow, those substances the presence of which is not tolerated by the Bacterium being called 'germicides' or 'antiseptics.' On account of the practical importance of destroying or inhibiting the development of putrefactive and pathogenic Bacteria, a good deal of attention has been given to this subject by chemists, but unfortunately it is only recently in the laboratory of Koch [15] that experiments to determine the germicidal action of chemical substances have been made with the necessary discrimination of the species of Bacteria which were the subject of experiment. The fact is now definitely established that some species of Bacteria are killed by chemical substances which do not injuriously affect others, and that the amount of such substances which is effective varies in the case of different species. The inquiry has only as yet been commenced, but it is of immense practical importance, since it may be possible to discover 'germicides' of a generally innocuous character which are specific poisons for certain disease-producing Bacteria, whilst harmless to other Bacteria and harmless to the higher animals in whose tissues the pathogenic Bacteria flourish. Thus weak solutions of quinine sulphate are poisonous to the *Bacterium ureæ*, whilst not injurious to putrefactive Bacteria. Such a solution can be injected into the human bladder without causing irritation, and thus the inflammation resulting from the ammoniacal decomposition of the urine in the bladder by Bacterium ureæ, which sometimes gains access thereto, can be entirely arrested. In this inquiry the difference between actual destruction of the life of the Bacteria, and their arrest or inhibition of growth due to the presence of the antiseptic chemical, have to be distinguished. It is also needful to inquire how far such 'antiseptics,' without killing or inhibiting Bacteria, may modify the physiological processes and chemical results brought about by the latter. The most powerful and generally effective poison for Bacteria appears to be corrosive sublimate. The presence of as little as 1 in 10,000 of this salt in a nutrient fluid has been found to kill Bacteria present. Phenol is also a general and powerful germicide. Boracic acid also and common salt in large quantities are effective. The nature of their action and their effectiveness in regard to different species of Bacteria have yet to be accurately determined. Antiseptic surgery, the future treatment of zymotic disease, and the preservation of perishable articles of food, depend upon the further discoveries of chemists in regard to this matter. It is not improbable that the most effective and useful germicides will be found in chemical substances which, like quinine, resemble those inhibitory products which are produced by the Bacteria themselves and act as the natural obstacles to their excessive multiplication. The more general question of the tolerance of or necessity for the presence on the one hand of free acid, on the other of free alkali in the nutrient fluids suited to different Bacteria, belongs here. It has been studied in regard to many Bacteria in a rough and ready way. Some Bacteria will not flourish in acid media, others will; but accurate quantitative investigations are still wanting.

The products of the activity of Bacteria.—When a species of [illegible] grows in a nutrient fluid of known chemical composition with access to a definite and limited volume of atmospheric oxygen—under given conditions of temperature, pressure, and illumination—certain chemical interchanges occur in the materials contained in the apparatus. These can be accurately determined in certain instances, and the variation of the quantity of change in relation to time can be stated. Various factors of the process, such as temperature, presence or absence of initial chemical substances, &c., can be varied, and the results stated and compared. In no case has such an experiment as yet been accurately made by a chemist. Nevertheless, we know roughly that, in the supposed experimental apparatus above indicated, there will be after a certain time an increase in the weight of mycoprotein and albumens existing in the form of Bacteria, and a corresponding diminution in the C, H, N, and O of the other material in the apparatus. Not only this, but we find certain new chemical compounds present outside the actual substance of the multiplied Bacteria which result from and accompany the growth and life of the particular species experimented upon. The same general statement is true of any higher organism in relation to its necessary pabulum; but whereas in large multicellular organisms the resulting products of the life of the organism are temporarily or permanently held within the mass of the body, in the minute unicellular Bacteria there is no taking in or envelopment of the materials to be acted upon by the living thing, but the organism gets into its food instead of

the food getting into it; consequently processes comparable to the digestive and even to the more deep-seated metabolic processes of higher organisms take place in the nutrient liquid in which the Bacterium lives, being initiated at the surface of the swarming cells constituting the colonies of these minute plants, and serving their economy equally as well as though they occurred in an alimentary canal or in a series of blood-vessels and tissue-spaces. The chemical changes induced by Bacteria should be studied from the same point of view as that taken by the physiologist in regard to the activities of the various cells of the tissues with their diverse and specific functions. We are not yet in a position to treat the subject from this standpoint but we can distinguish with more or less certainty results traceable to respiration, digestion, assimilation, secretion and excretion; the chemical correlatives of these processes are changes described as de-oxidation, oxidation, specific fermentations, specific syntheses.

The *obvious* results of the activity of Bacteria (setting aside the probably universal evolution of CO_2 and consumption of free O, common to the Bacteria and all living protoplasm) though by no means necessarily the most important in regard to their own physiology, are the production in the liquids in which they grow of (1) substances having distinctive smells and flavours; (2) substances having brilliant colours; (3) substances having eminently poisonous properties; to these may be added such remarkable results of oxidation as the manufacture of nitrates in soil, of acetic acid in vinegar factories, and the manifestation of light—the phosphorescence of decaying ... bones, and other organic refuse.

The chemical nature of the substances which are thus produced, the by-products which accompany them, and the nature of the processes by which they are originated, have not yet formed the subject of chemical investigation to any large extent. Such knowledge as we have is due to Pasteur [16], to Fitz [17], and one or two others.

It seems probable that we may distinguish amongst these results those which are due to synthesis, by the Bacterium acting on lower compounds taken into its substance, and those which are due to analysis resulting from the action of ferments and other agents secreted by the Bacteria and acting on surrounding material of a high degree of chemical complexity. Of the nature of these ferments we know nothing; their existence is hypothetical but highly probable. To the first category belong certainly many of the brilliant pigments which the Bacteria produce; in most cases these pigments are soluble and pass out from the protoplasm into the surrounding water. In *Bacterium rubescens* the wine-red pigment is not soluble, and remains where it is manufactured in the cells of the plant. The remarkable smelling substances formed by putrescent Bacteria also belong to this group of built-up products, and it is probable that the poisonous products of some pathogenous Bacteria, though not of all, are thus elaborated. The chief experimental reason which we have for concluding that these bodies are built up by the Bacterium from lower compounds is this, that they are formed when the Bacterium is cultivated in a pure solution of ammonium tartrate (with traces of mineral salts) often called Pasteur's or Cohn's solution. Thus the Bacterium of blue milk can be grown and made to produce its blue colour from ammonium tartrate, the Bacterium of green pus similarly, and many of the chromogenic Micrococci, whilst some of the specially active putrefactive Bacteria manufacture foul-smelling products from the same salt when experimentally nourished with it.

In regard to the second group, that of substances resulting from a breaking down of higher chemical bodies brought into relation with the Bacterium (and that probably by the action of a secreted ferment which may be minute in amount and possibly never separated from the surface of the Bacterium-cell), we have to note first of all that the ferment itself belongs to the previous group. Secondly, that various species of Bacteria have been shown to produce ethylic and other alcohols in this way—from sugar and similar bodies—as does the yeast-plant (Saccharomyces). Fitz [17] has shown that a certain Bacterium converts glycerin into ethyl alcohol, whilst another converts it into butyl alcohol. Other Bacteria have been shown to convert sugar into gum or into mannite, producing the so-called 'ropy fermentation' of syrups, wine, and beer. Urea is converted into carbonate of ammonia, hippuric acid into benzoic acid and glycocoll. Albumens are broken down into bodies which have not been determined in many cases, but include the ptomaïnes, neuridine, and trimethylvinyl-ammonium hydrate. Various Bacteria as well as the specific *B. lactici*, produce small quantities of lactic acid from various substances, such as grape-sugar, milk sugar, and glycerin, whilst possessing other ferment-producing action also. Butyric acid is frequently produced in these processes by other Bacteria as well as by the B. butyricum of cheese-factories. Exact knowledge is, however, sadly deficient in these matters, owing to the fact that hitherto chemists have not been careful to ascertain what species of Bacterium is present in the fermentations studied by them. Owing to this we do not yet know whether in different nourishing fluids and under different conditions of access of oxygen and of temperature, the *same* Bacterium can produce different fermentations. Such knowledge as we have tends to a positive answer to the above question. One of the best researches with a known species of Bacterium is that of Vandevelde [18], on the hay bacillus (B. subtile).

Since it is probable that there is this change of chemical activity under changed conditions, it is also probable that a Bacterium which is harmless under ordinary conditions of growth may, when specially cultivated in albuminous media, acquire the property of living in the animal body as a parasite, and there cause deadly disease by its fermentative action, or by the secretion of poisonous products. Buchner [19], starting from this theoretical consideration, has endeavoured to produce the deadly *B. anthracis* of splenic fever from the hay bacillus (*B. subtile*), and conversely to restore the parasitic form by cultivation to the primitive state. His experi-

ments, though of extreme interest, are not conclusive.

It is difficult to hazard a guess as to whether the poisonous effects of any given Bacterium proved to be concerned in the production of disease, are due to the secretion of a poison by the Bacterium or to the production of one by its fermentative action upon the constituents of the blood, tissues, or intestinal contents. The chemical theory of the antidotal action of inoculation with various 'vaccine' cultivations, which is that favoured by their chief discoverer and investigator, M. Pasteur, would seem to involve the hypothesis that whilst the effective poison is a secretion of the Bacterium, the antidotal material is a chemical compound resulting from the fermentative action of the Bacterium, quite distinct from the poison. This fermentation-product by its accumulation inhibits the development of the Bacterium as alcohol inhibits the further growth of the yeast plant by the fermentative action of which it has been formed. The phagocyte theory of Metschnikow [20] in relation to preventive inoculation does not involve this distinction (see below).

The oxidising action of Bacteria must be considered merely as a special form of their fermentative action. By the latter they produce intermediate chemical substances which are readily oxidised by the free atmospheric oxygen. It is probably thus that acetification proceeds when *B. aceti* converts ethylic alcohol into vinegar or when organic nitrogenous bodies and ammonia in the soil are converted into nitrites and nitrates. There is no evidence of a specific oxidising action on the part of the Bacterium. The phosphorescent substance produced in stale fish, old bones, meat, &c., under certain conditions by certain Bacteria (as yet not precisely determined) may be regarded as an example of one of these intermediate oxidisable substances. The oxidation in this case is accompanied by the evolution of light.

Special Study of the Occurrence and Distribution of Bacteria in the Atmosphere and in Potable Waters.—The ubiquity of Bacteria has been demonstrated by the use of sterilised nutrient fluids. If such a fluid be touched by a glass rod or by the finger or by any surface not chemically cleansed, Bacteria are conveyed into the fluid and multiply there with enormous rapidity. Gelatin has been used as a means of studying the number of Bacteria present in the atmosphere or in a sample of water (*v.* Percy Frankland's researches [21]). However modified, the process is essentially this: a given volume of air is passed through a liquid so as to arrest all Bacteria previously floating in the air. The liquid is then mixed with gelatin, warmed to liquefy the gelatin, and rapidly cooled as a thin layer on a plate. The Bacteria develop at various separate points in the gelatin, giving rise to spherical growths or nests. These are then counted, and the species present may be discriminated by further cultivation. Where water is the subject of investigation the gelatin is directly mixed with a given volume of the water. The results thus obtained have only a subordinate value from the point of view of the hygienist. The majority of Bacteria are perfectly innocuous, and their presence is not—as has been too readily assumed—an indication of the probable presence of pathogenic Bacteria. No such natural association of pathogenic and innocuous Bacteria in definite proportions has been ascertained, and its assumption is not warranted. It is necessary in all cases, if the results are to have hygienic value, to distinguish the kinds or species of Bacteria present and to ascertain their properties. Further, it is quite certain that all species of Bacteria will not flourish in gelatin even when mixed with peptone or such bodies. For instance, one of the most important pathogenic Bacteria—that concerned in tubercular consumption—will not do so. A special pabulum is needed for this Bacterium, and its presence would not be indicated by the ordinary gelatin cultivation of the contents of a given volume of air. Hence it seems necessary that in addition to careful discrimination of the Bacteria obtained by such experiments on atmospheric and aquatic distribution, there should be a systematic use of various cultivating media for the purpose of demonstrating the presence of various kinds of Bacteria. No doubt many kinds can be secured by the peptonised gelatin method, but if the results of such studies are to have any qualitative hygienic significance, other cultivating media must be simultaneously made use of. All the work at present done on this subject requires doing afresh from this point of view.

Special Study of Pathogenic Bacteria.—A large number of most important observations have been made of late years by pathologists—especially by Lister, Pasteur, Koch, Klein, and their pupils—demonstrating not only the presence of Bacteria in the blood and tissues of man and other animals when in a state of disease, but also proving in a certain number of cases that the Bacteria are the cause of specific disease.* The proof, which is sufficient, and has been furnished in a limited number of instances, consists in—1. The constant presence of a definite form of Bacterium in the diseased animal and in the specially-diseased parts of it. 2. Its successful removal from the diseased animal, and its pure cultivation on media free from all contamination by particles of the diseased animal.—3. The experimental introduction of the cultivated Bacterium into the body of a healthy animal liable to the disease in question but free from it.—4. The subsequent development of the disease in the inoculated animal. This proof has been furnished in regard to the connection of *B. anthracis* with splenic fever in cattle and sheep, and malignant pustule in man; in regard to *B. tuberculosis* and consumption or phthisis in man and animals; in regard to *B. choleræ gallinæ* and the cholera of fowls; in regard to *Micrococcus erysipelatosus* and erysipelas of man; in regard to certain Bacteria and septicæmic and pyæmic conditions in rats, mice, rabbits, and birds; and in regard to some other diseases of animals. Such a connection is strongly suspected, but not yet proved in the complete manner formulated above in regard to certain observed Bacteria or Micrococci, and the following diseases, viz. small-pox, scarlatina, diphtheria, typhoid fever, cholera asiatica, malaria, yellow-fever, gonorrhœa, &c. The first definite researches in this direction, which were immediately accompanied by practical results of enor-

mous value, were those of Sir Joseph Lister, who showed that the blood-poisoning so frequent in crowded hospitals after surgical operations was due to the access of Bacteria to the wounds where they multiplied and manufactured poisonous products (sepsine, ptomaines?) which were absorbed into the blood. Lister adopted measures for preventing the access of these Bacteria, chiefly by the use of phenol and great cleanliness in instruments, dressings, &c., and thus established the antiseptic system of surgery.

It is remarkable that the researches which have been made on the relation of Bacteria to disease have been mostly of a purely empirical character. Almost the only investigator who has carried the matter further (and with the most brilliant results) is the French chemist Pasteur. The fact is that the question as to what the Bacteria do after entering an animal body is, like the question of their action on substances external to the body, essentially a chemical one. Following up the observations of Toussaint, Pasteur [22] was led to the discovery that the *Bacterium anthracis* when cultivated in broth could be made to assume a condition in which its virulence was greatly diminished. Nevertheless when introduced into the tissues of a sheep, the cultivated Bacterium multiplied, and as a consequence of its growth rendered the sheep so treated resistant to the attacks of the virulent Bacterium anthracis taken from another animal's blood.

It was known that an animal which had survived an attack of the virulent *B. anthracis* was thereby rendered 'immune' to subsequent attacks, just as one attack of small-pox renders its survivor 'immune' to that disease. Pasteur conceived the theory that the Bacterium causing the disease in all such cases produces as a by-product—independent of its specific poison—a chemical substance which inhibits its further growth (as in the case of the alcohol produced by the yeast-plant) and that this substance remaining in the animal body protects it from being the seat of further growth of the pathogenic Bacterium. The modified cultivated variety of B. anthracis equally produces this substance, and consequently acts as a protective against the incursions of the virulent form. Similarly cow-pox is to be regarded as the result of the growth of a modified small-pox Micrococcus, and thus the protective effects of inoculation with cow-pox are to be explained. Applying this conception Pasteur has successfully protected fowls against fowl-cholera, and has been led to his greatest triumph, the protection by inoculation against rabies and the successful treatment of persons bitten by rabid dogs.

It is extremely interesting and important to observe that the discoveries which have been made in this subject are due to chemical conceptions. Nevertheless there is much probability in the view put forward by Metschnikow (a distinguished zoologist, now director of the Bacteriological Institute of Odessa) to the effect that protective inoculation does not depend upon the development within the inoculated animal of a germicidal poison, resulting from the growth of the very germ which is killed or inhibited by that poison, but is rather due to the education of the living tissues, and especially of the white corpuscles of the blood, which, he has proved, attack and feed upon Bacteria which are multiplying in the blood and tissues. This property of the white corpuscles leads Metschnikow to term them 'phagocytes,' and, according to him, preventive inoculation depends for its efficacy on the fact that, having learnt to resist and destroy a weaker modification of a pathogenous Bacterium, they are able to deal subsequently with the more virulent variety; whilst it has been suggested that in the struggle between the phagocytes and the inoculated modified Bacteria, there must be a survival of the fittest and a consequent strengthening of the later generations of phagocytes in the protected animal.

However this may be, it is obvious that both the direct study of the chemical history of pathogenic Bacteria and the indirect suggestions derived from further knowledge of the chemical history of Bacteria of all kinds, are of an importance to human life and health which cannot be over-estimated.

In connection with the study of the pathogenic Bacteria which attack man, it is necessary to insist that at present no one has attempted to determine the various kinds of Bacteria which are normally present on the surface of the human body, in the mouth, stomach, and intestines. There appear to be twelve or more present in the healthy human mouth (*v.* Vignal, [23]). So strangely has this matter been neglected that Koch of Berlin was ignorant, when he discovered the so-called 'comma-bacillus' in the intestines of choleraic subjects in India, that an identical form occurs in the healthy human mouth, as shown by Lewis [24].

Spontaneous generation or abiogenesis.—Twenty years ago experiments and observations were brought forward by various more or less competent observers [25] which were interpreted as proving the sudden formation of Bacteria as living things in fluids containing the elements of protoplasm where no germ or living thing previously existed. It is sufficient to say here that these views had a valuable effect in stimulating the investigation of the life-conditions and activities of the Bacteria, but have been definitely proved to be erroneous and to have arisen from the imperfect state of knowledge as to the ubiquity of Bacteria and the power to resist the destructive effect of boiling water possessed by the spores of Bacterium subtile—the hay bacillus.

Conclusion.—An endless field of investigation is open in connection with the Bacteria. It seems certain that in the near future we shall be able to control the disease-producing forms, whilst the suggestion presses itself that it may be possible to cultivate and intensify the activities of those which act as scavengers and even to lead some by appropriate methods to the acquirement of new powers, or to the development of activities at present scarcely recognised. There is no reason, from the point of view of the biologist, why these lowest plants should not be cultivated and specialised as breeds and varieties for the service of mankind, as the peach and the strawberry, the wheat and the cabbage have been.

E. R. L.

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BALANCE *v.* ANALYSIS.

BALATA. A substance resembling caoutchouc and gutta-percha, obtained from the dried milky juice of the Bully-tree (*Sapota Muelleri*) (Sperling, *Z.* [2] 5, 480).

BALSAM. This term was originally confined to a single substance called Balm of Gilead or Balsam of Judea, but is now employed generally to denote any liquid resin with aromatic odour. They are composed of solid resins mixed with essential oils. Balsams of Peru, Tolu, Liquidambar, and Storax, contain cinnamic acid; Copaiba balsam, Mecca balsam, and turpentine, do not.

BARABANIC ACID *v.* PARABANIC ACID.

BAPHIIN $(C_{12}H_{10}O_4)_n$. Extracted by ether from barwood (*Baphia nitida*). Plates or needles (from ether), insol. water, v. sl. sol. benzene. Its alcoholic solution is turned red by air. Boiling aqueous KOH converts it into baphic acid $C_{24}H_{22}O_8$ (?), baphnitin $(C_6H_6O)_n$, and baphnitone, $C_{26}H_{26}O_6$. The latter gives a tri-bromo- derivative $C_{26}H_{23}Br_3O_6$.

BAPTISIA TINCTORIA. The root of this plant contains a crystalline alkaloid (Greene, *Ph.* [3] 10, 584).

BARBALOIN *v.* ALOÏN, p. 140.

BARBATIC ACID $C_{19}H_{20}O_7$. [186°]. Occurs, together with usnic acid, in a lichen, *Usnea barbata* (Stenhouse a. Groves, *C. J.* 37, 405; *A.* 203, 302). Needles or plates (from benzene). Decomposed by boiling milk of lime into CO_2 and (β)-orcin.

BARBITURIC ACID

$$C_4H_4N_2O_3 \ \textit{i.e.}\ CH_2\!<\!\begin{matrix}CO.NH\\CO.NH\end{matrix}\!>\!CO.$$

Malonyl-urea. Formed by heating malonic acid with urea and $POCl_3$ at 100° (Grimaux, *C. R.* 88, 85; *A. Ch.* [5] 17, 276), or by reducing di-bromo-barbituric acid with sodium amalgam or HI. Prepared by heating alloxantin (1 pt.) with H_2SO_4 (3 or 4 pts.) at 100° as long as SO_2 comes off. The product is poured into water.

Properties.—Trimetric prisms (containing 2aq) from water. Sl. sol. cold, v. sol. hot, water.

Reactions.—1. Boiling *aqueous potash* forms malonic acid and urea (CO_2 and NH_3).—2. HNO_3 forms nitro-barbituric (dilituric) acid.—3. KNO_2 forms nitroso barbituric (violuric) acid.—4. Br forms di-bromo-barbituric acid.—5. *Heated with glycerin* it forms dibarbituric acid, urea, and ammonium malonurate.—6. *Cyanogen* forms a compound $C_4H_4N_2O_3(CN)_2$aq, whence potash forms cyanuromalic acid.

Salts.—NH_4HA'': needles, v. sl. sol. cold water.—Na_2A'' 2aq.—KHA''.—$BaH_2A''_2$ 2aq.—PbA''.—$CuH_2A''_2$ 3aq.—$AgHA''$.—Ag_2A''.

Acetyl derivative $C_4H_3AcN_2O_3$. A by-product in the preparation of barbituric acid from urea, malonic acid, and $POCl_3$. Powder, sol. hot water.

Di-methyl derivatives.—I. *Malonyl-dimethyl-urea* $CO\!<\!\begin{matrix}NMe.CO\\NMe.CO\end{matrix}\!>\!CH_2$. [123°]. From malonic acid, di-methyl-urea and PCl_3, or from di-methyl-urea and cyano-acetyl chloride, $CN.CH_2.CO.Cl$ (Mulder, *B.* 12, 466). Flat needles, v. sol. water. Forms a di-bromo-derivative [175°-180°].

II. *Di-methyl malonyl-urea*

$CO\!<\!\begin{matrix}NH.CO\\NH.CO\end{matrix}\!>\!CMe_2$. [265°]. From silver barbiturate and MeI (Conrad a. Guthzeit, *B.* 14, 1643) or from di-methyl-malonic acid, urea, and $POCl_3$ (Thorne, *C. J.* 39, 545). Plates (from water). V. sl. sol. cold water. Boiling KOH forms di-methyl-malonic acid.

Salt.—Ag_2A'' ½aq.

Ethyl derivative $CO\!<\!\begin{matrix}NH.CO\\NH.CO\end{matrix}\!>\!CHEt$. [190°]. From ethyl-malonic acid, $POCl_3$, and urea. Gives a bromo-derivative.

Di-ethyl derivative $CO\!<\!\begin{matrix}NH.CO\\NH.CO\end{matrix}\!>\!CEt_2$. [182°]. From silver barbiturate and EtI.

Benzyl derivative
$CO<\begin{smallmatrix}NH.CO\\NH.CO\end{smallmatrix}>CH.CH_2Ph$. [206°]. From benzyl-malonic acid, $POCl_3$, and urea.

Additional References.—Finck, *A.* 132, 304; Baeyer, *A.* 130, 136; Conrad a. Guthzeit, *B.* 14, 1643; 15, 2844.

Di-barbituric acid $C_8H_6N_4O_5$. The ammonium salt is formed by heating barbituric acid with glycerin at 150°. The acid is an insoluble powder; it gives a di-bromo- derivative.

Salts.—NH_4HA''.—Na_2A'' 2aq.—KHA'' *x*aq (Baeyer, *A.* 130, 145).

BARIUM. Ba. At. w. 136·8. Mol. w. unknown, as V.D. not determined. Very little known of properties; doubtful if approximately pure Ba has yet been obtained. S.G. abt. 3·5–4 (sinks in H_2SO_4). S.V.S. abt. 36·5. Chief lines in spectrum are 5850, 5538, 4934, 4553, 8140 (Huggins, *T.* 154, 139).

Occurrence.—Not as metal; chiefly as sulphate (*heavy spar*), and carbonate (*witherite*); also as silicate in combination with silicates of Sr, K, or Al, and as oxide in combination with oxide of Mn. Ba compounds occur in many mineral waters; in the ashes of certain plants (Eckart, *A.* 100, 294); and in small quantities in sea water (Dieulafait, *A. Ch.* [5] 15, 540).

Formation.—An amalgam of Ba and Hg is prepared in several ways:—(*a*) by electrolysing $BaCl_2$ mixed with a little very dilute HClAq, using an amalgamated Pt wire as negative electrode (Bunsen, *A.* 92, 248); (*b*) by electrolysing moist BaO using Hg and Pt as electrodes (Davy, *T.* 1808. 303); (*c*) by bringing hot BaO or $BaCl_2$ into contact with vapour of K, and treating the product with Hg, or by heating BaO with Na and treating with Hg (Kern, *C. N.* 31, 244); (*d*) by the action of Na amalgam on conc. warm $BaCl_2$Aq (Crookes, *C. N.* 6, 194). By heating Ba amalgam in an atmosphere of H, or of hydrocarbon vapours, metallic Ba was supposed to be obtained; but Donath (*B.* 12, 745) asserts that it is impossible to remove all the Hg even at a white heat, and that the residue contains as much as 62 to 77 p.c. Hg.

Preparation.—By electrolysis of fused $BaCl_2$ mixed with NH_4Cl, in a porcelain crucible in an atmosphere of H; the positive electrode consisting of a cylinder of coke, the negative of an iron wire (Matthiessen, *C. J.* 8, 294).

Properties and Reactions.—It is very doubtful whether the properties enumerated by different chemists as characteristic of Ba were determined by experiments made on even approximately pure metal. Davy described Ba as silver-white; Bunsen and Matthiessen as a golden yellow, slightly lustrous, somewhat malleable, metal, which melts at a red heat, but cannot be distilled. It is very easily oxidised, decomposes cold H_2O readily, and burns in the oxyhydrogen flame. As no gaseous compounds of Ba have as yet been obtained, and as the spec. heat of the metal has not been determined, the value to be given to its atomic weight, the combining weight or equivalent having been determined, is arrived at chiefly by considering the analogies between the compounds of Ba and those of other allied elements, chiefly Ca, Sr, Mg, Zn, and Cd. These analogies lead to the formulæ BaX and BaY_2 for the compounds of Ba, where X = O, S, SO_4, CO_3, &c., and Y = Cl, NO_3, ClO_3, &c.; these compounds belong to one series. The valency of the atom of Ba in gaseous molecules is unknown. That the atomic weight of Ba is represented by a number the most probable value of which is about 136·8, provided the composition of the Ba compounds is expressed by the general formula BaX_2, where X = a monovalent atom or group of atoms, was established chiefly by analyses of barium chloride conducted by Marignac (*A.* 68, 215; 106, 165) and Dumas (*A. Ch.* [3] 55, 137). Ba reacts as a strongly positive metal; the salts obtained by replacing H of acids by Ba are stable and well marked; BaO and BaO_2H_2, BaS and BaS_2H_2, exhibit no acidic characters; BaO_2H_2 is distinctly alkaline, its heat of neutralisation is the same as that of soda and potash (*Th.* 1, 332) $[BaO^2H^2Aq, H^2SO^4Aq] = 31,150$; $[BaO^2H^2Aq, 2HClAq] = 27,640$. Ba combines with O and the halogens with production of much heat and formation of very stable compounds:—$[Ba,O]$ = abt. 124 000; $[Ba,Cl^2] = 194,700$; $[Ba,Br^2] = 170,000$ (*Th.* 3, 266); these numbers are approximate only; they were determined indirectly, except that for BaO, but the Ba used was not free from Hg. Barium is very closely related to Ca and Sr, and less closely to Mg (*v.* art. ALKALINE EARTHS, METALS OF THE).

Baryta was obtained by Scheele in 1774 from heavy spar; Davy in 1808 decomposed baryta by electrolysis; the metal was obtained approximately pure in 1855 by Bunsen and Matthiessen.

Combinations.—Very few compounds of Ba have been formed directly from the metal. It forms alloys with a few metals; that with *mercury* (*v. supra, Formation*) is a silver-white body which rapidly decomposes water and cannot be separated into Ba and Hg by heat alone. Beketoff (*A.* 110, 375) obtained an alloy with *aluminium*, as a greyish solid with a tinge of yellow, by heating Al with BaO_2H_2 and a little $BaCl_2$; it decomposed H_2O rapidly, but the water did not acquire an alkaline reaction. Caron described alloys of Ba with lead, bismuth, antimony, &c., obtained by the action of alloys of these metals with Na on molten $BaCl_2$ (*A.* 111, 114).

Detection.—Many salts of Ba are soluble in water; some are insoluble; aqueous solutions of Ba salts are ppd. by conc. HClAq or conc. HNO_3Aq. Insoluble Ba salts are decomposed by fusion with alkaline carbonates, giving $BaCO_3$ which dissolves in dilute acids. Fusible salts of Ba impart a pale yellowish-green colour to the non-luminous flame; the colour appears blue-green through a green glass. The emission-spectrum of Ba is characteristic; it contains very many lines in the green; about $\frac{1}{1000}$ mgm. Ba may be detected by the spectroscope. *Dilute sulphuric acid*, or a *dilute aqueous solution of sulphates*, ppt. white $BaSO_4$, insoluble in alkalis and dilute acids; 1 part $Ba.2NO_3$ in 100,000 parts of water gives an immediate pp.; one part in 400,000 gives a cloudiness on standing. By this reaction Ba salts are distinguished from Ca salts, and to some extent from salts of Sr.

Estimation.—1. Ba is usually determined as $BaSO_4$, which is ppd. from fairly conc. solutions, containing a little HCl or HNO_3, by dilute H_2SO_4Aq; the pp. is collected, well washed,

and strongly heated, before weighing. If salts of Ca are present, $CaSO_4$ may be removed from the pp. by long washing with very dilute HClAq, or by digesting with $Na_2S_2O_3Aq$ (Diehl, *J. pr.* 79, 80) which dissolves $CaSO_4$ but not $BaSO_4$. $PbSO_4$, if present, may be removed from the pp. by washing with solution of potash, or of ammonium tartrate.—2. In presence of salts of Ca and Sr, Ba is best estimated as $BaSiF_6$, which is ppd. by freshly prepared H_2SiF_6Aq, followed by alcohol; after standing 12 hours, the pp. is collected, washed with a mixture of equal volumes of alcohol and water, dried at 100°, and weighed (*v.* also Rose, *P.* 95, 286, 299, 427).

Barium, alloys of, *v.* BARIUM; *Combinations.*

Barium, antimonates of, *v.* ANTIMONATES, under ANTIMONY, ACIDS OF.

Barium, arsenates of, *v.* ARSENATES, under ARSENIC, ACIDS OF.

Barium, arsenites of, *v.* ARSENITES, under ARSENIC, ACIDS OF.

Barium, bromide of. $BaBr_2$. Mol. w. unknown, as compound has not been gasified. [abt. 812°] (Carnelley, *C. J.* 33, 280). S.G. 4·23 (Schiff, *A.* 108, 21). H.F. $[Ba,Br^2] = 169,960$; $[Ba,Br^2,Aq] = 174,940$ (*Th.* 3, 266).

Formation.—1. By acting on BaO_2H_2 or BaS, with HBrAq.—2. By adding BaS to an aqueous solution of Br.—3. Along with $BaBrO_3$, by the action of Br on BaO_2H_2Aq.

Preparation.—Aqueous HBr is neutralised by pure $BaCO_3$, the liquid is boiled down and allowed to crystallise, and the crystals of $BaBr_2.2H_2O$ are heated in a stream of dry air to 100°.

Properties and Reactions.—Crystallises with $2H_2O$ in white trimetric plates (Rammelsberg, *P.* 55, 237); according to Hauer (*J. pr.* 80, 230) and Werther (*ibid.* 91, 167) the crystals are monoclinic; the hydrated salt is perhaps dimorphous. H.F. $[BaBr^2,2H^2O] = 9,110$. $[Ba,Br^2,2H^2O] = 179,070$ (*Th.* 3, 266). Heated to 75°, $BaBr_2.H_2O$ remains, and at 100° $BaBr_2$ is obtained. The hydrate $BaBr_2.2H_2O$ is soluble in water. S. (0°) 98; (20°) 104; (40°) 114; (60°) 123; (80°) 135; (100°) 149. It is also easily soluble in alcohol. S.G. 3·69 (Schiff, *A.* 108, 21). $BaBr_2$ is completely decomposed by heating to redness in dry O (Schulze, *J. pr.* [2] 21, 407). When conc. aqueous solutions of $BaBr_2$ and BaO are mixed so that the salts are present in the ratio $BaBr_2$:BaO, crystals of $BaBr_2.BaO.5H_2O$ ($= BaBrOH.2H_2O$) separate out (Bechmann, *J. pr.* [2] 26, 388 and 474).

Barium bromide, hydrated, *v.* BARIUM, BROMIDE OF; *Preparation.*

Barium, chloride of. $BaCl_2$. Mol. w. unknown, as compound has not been gasified. [abt. 860°, Carnelley]. S.G. 3·75–3·89 (Schröder, *P.* 107, 113). S.H. (16°–47°) ·0902 (Kopp, *T.* 155, 71); (14°–98°) ·0896 (Regnault, *A. Ch.* [3] 1, 129). S. (5°) 32·2; (30°) 38·2; (50°) 43·6; (80°) 52·4; (100°) 58·8 (Mulder; *v.* Michaelis' *Lehrbuch der Anorgan. Chem.* 3, 900). S. (alcohol 99 p.c.: 14°) ·01; (alcohol at B.P.) ·06 (Fresenius, *A.* 59, 127). H.F. $[Ba,Cl^2] = 194,740$; $[Ba,Cl^2,Aq] = 196,810$ (Thomsen). The following data apply to the hydrate $BaCl_2.2H_2O$: S.G. 3·052 (Schiff, *A.* 108, 21). S.H. (18°–46°) ·171 (Kopp, *T.* 155, 71). S. (15°) 43·5; (105°) 78. H.F. $[Ba,Cl^2,2H^2O] = 201,740$; $[Ba,Cl^2,2H^2O] = 7,000$ (*Th.* 3, 266). C.E. (cub. abt. 15°–200°) ·0000548 (Playfair a. Joule, *C. J.* 1, 121).

Formation.—1. By the action of Cl on hot BaO (Weber, *P.* 112, 619).—2. By passing HCl over hot BaO; light is evolved as well as heat: or by adding conc. HClAq to BaO, boiling down, and drying at 100°.—3. By dissolving BaS in conc. HClAq, boiling down, and drying at 100°.

Preparation.—1. Powdered *witherite* ($BaCO_3$) is added little by little to HClAq; the solution is digested in absence of air with more $BaCO_3$ (to remove iron, &c.), and is then poured off, evaporated to dryness, and the residue heated to 100° for some time.—2. Two parts of finely powdered heavy spar ($BaSO_4$) are heated in a crucible to redness with 1 part dry $CaCl_2$ and 2 parts iron filings; the fused mass is digested for a short time with 6-8 parts boiling water (by long digestion $BaSO_4$ and $CaCl_2$ are re-formed), the liquid is filtered from FeS, CaS, and undecomposed $BaSO_4$, made slightly acid by HClAq, and evaporated to dryness at 100°.—3. The solution of $MnCl_2$ which is obtained in making Cl from MnO_2 is neutralised by $BaCO_3$ or $CaCO_3$ and evaporated to dryness; the residue is heated with heavy spar and coal; the mass is lixiviated (MnS, FeS, and some $BaSO_4$ remain), the liquid is treated with a little $MnCl_2Aq$ to decompose any BaS present, HClAq is added, and the whole is evaporated to dryness (Kuhlmann, *C. R.* 47, 403, 464, 674).

Properties.—White salt, easily soluble in water, $[BaCl^2,Aq] = 2,070$ (*Th.* 3, 266); slightly soluble in alcohol (*v. supra*); solution has a bitter taste and is poisonous. Melts at red heat and cools to an opaque mass.

Reactions.—1. Heated in *steam*, HCl is evolved, and residue has an alkaline reaction.—2. Partly oxidised by fusion with *potassium chlorate*, but unchanged by heating in dry *oxygen* (Schulze, *J. pr.* [2] 21, 407).—3. Completely decomposed by fusion with *silicates*.

Combinations.—1. Conc. solution of $BaCl_2$ mixed with conc. BaOAq pps. thin transparent plates of $BaCl_2.BaO.5H_2O$ ($= BaClOH.2H_2O$) (Bechmann, *J. pr.* [2] 26, 388, 474).—2. Combines with *water* with production of heat, $[BaCl^2,2H^2O] = 7,000$, to form the hydrate $BaCl_2.2H_2O$. This hydrate crystallises in white flat trimetric plates, which are not efflorescent; they lose $2H_2O$ at 100°, but take it up again in moist air. A conc. solution is decomposed to $Ba.2NO_3$ and NaCl by heating with $NaNO_3$.

Barium chloride, hydrated, *v.* BARIUM, CHLORIDE OF; *Combinations*, No. 2.

Barium, cyanide of. $Ba(CN)_2$. Obtained by action of HCNAq on BaO_2H_2 (*v.* CYANIDES).

Barium, fluochloride of. BaFCl (*v.* BARIUM, FLUORIDE OF).

Barium, fluoride of. BaF_2. Mol. w. unknown, as compound has not been gasified. [abt. 908°] (Carnelley, *C. J.* 33, 280). S.G. 4·58 (Bödeker).

Preparation.—1. By ppg. $Ba2NO_3Aq$ by NaFAq.—2. By the action of HFAq on BaOAq, or on freshly ppd. $BaCO_3$, and evaporating. The former action is attended with the production of much heat; Guntz (*A. Ch.* [6] 3, 5) gives the values $[BaOAq, 2HFAq] = 34,800$; and

$[BaO^2H^2, 2HF] = 71{,}400$ (solid BaF_2 is produced by action of gaseous HF on solid BaO_2H_2).

Properties and Reactions.—White, finely granular, crystals; scarcely soluble in water but easily in HNO_3Aq, HClAq, and HFAq. Not decomposed by heat alone.

Combinations.—1. With $BaCl_2$ to form $BaF_2.BaCl_2$ (= BaFCl); obtained by adding NH_3Aq to a solution of BaF_2 in HClAq; also by fusing 1 part NaF with 6-8 parts $BaCl_2$, and digesting with water; also by adding KFAq to $BaCl_2Aq$ and evaporating. Forms white granular crystals, more soluble in water than BaF_2: partly decomposed, with loss of $BaCl_2$, by long-continued washing with water.—2. With BF_3 to form $BaF_2.2BF_3.2H_2O$ (= $Ba(BF_4)_2.2H_2O$); obtained by acting on $BaCO_3$ with HBF_4Aq, and evaporating; boric acid separates, and afterwards the double salt (*v.* BOROFLUORIDES under BORON, FLUORIDE OF).—3. With SiF_4 to form $BaF_2.SiF_4$ (= $BaSiF_6$); obtained by adding H_2SiF_6Aq to a solution of a Ba salt. White solid, very slightly soluble in cold water—S. (17°) ·03—and only slightly soluble in HClAq. S.G. 4·28. Leaves BaF_2 when heated; heated with NH_4Cl gives residue of $BaCl_2$ (Stolba, *J. pr.* 96, 22) (*v.* SILICOFLUORIDES, under SILICON, FLUORIDE OF).

Barium, hydroxide of. BaO_2H_2 (*Caustic baryta*). Mol. w. unknown, as compound has not been gasified. S.G. 4·495 (Filhol, *A. Ch.* [3] 21, 415). S. (0°) 1·5, (5°) 1·75, (10°) 2·22, (15°) 2·89, (20°) 3·48, (25°) 4·19, (30°) 5·0, (35°) 6·17, (40°) 7·36, (45°) 9·12, (50°) 11·75, (55°) 14·71, (60°) 18·76, (65°) 24·67, (70°) 31·9, (75°) 56·85, (80°) 90·77 (Rosenstihel a. Rühlmann, *J.* 1870. 314). H.F. $[Ba, O, H^2O] = 146{,}500$, value only approximate; $[BaO, H^2O] = 22{,}260$ (*Th.* 3, 266).

Formation.—1. By heating heavy spar with carbon, dissolving BaS formed in hot water, filtering, adding CuO or ZnO to decompose the BaS, filtering, evaporating to dryness, and heating to redness (Müller, *J. pr.* 82, 52; Stahlschmidt, *D. P. J.* 182, 30; Nicklès, *W. J.* 1869. 274).—2. By heating Fe with $Ba.2NO_3$ to redness, dissolving in water, filtering, evaporating, and heating the residue.—3. By the action of steam on $BaCO_3$ (Lenoir, *W. J.* 1867. 256).

Preparation.—1. Water is added little by little to BaO (*q. v.*); the product is heated to dull redness in a silver dish.—2. Aqueous solution of pure NaOH, S.G. about 1·1 to 1·15, the quantity of NaOH in which is accurately known, is heated to boiling, a quantity of powdered $Ba2NO_3$ is added equivalent to the NaOH used, the liquid is boiled for a little, if solution is not complete water is added, the hot liquid is filtered quickly and allowed to cool in a closed vessel when crystals of $BaO_2H_2.8H_2O$ are deposited; these crystals are separated, recrystallised from boiling water, and heated gradually to redness in a silver dish (Mohr, *Ar. Ph.* [2] 88, 38).

Properties and Reactions.—A white powder, dissolving in water (*v. supra*) to form an alkaline, caustic, liquid; melts at a full red heat and crystallises on cooling; not decomposed by heat alone, but by heating in a stream of air BaO and H_2O are produced. Aqueous solution is markedly alkaline, and neutralises acids with production of same quantity of heat as KOHAq and NaOHAq (*Th.* 1, 332). Does not absorb Cl, except in presence of H_2O; action is then probably $6BaOAq + 6Cl_2 = 5BaCl_2Aq + Ba(ClO_3)_2Aq$ (Weisberg, *B.* 12, 846). Is not acted on by CO_2 (Scheibler, *B.* 19, 1973).

Combinations.—With *water* with production of heat $[BaO^2H^2, 8H^2O] = 27{,}470$ (*Th.* 3, 266) to form crystals of $BaO_2H_2.8H_2O$ (Beckmann, *J. pr.* [2] 26, 388, and 474; Filhol found $7H_2O$, Noad and others $9H_2O$). (For preparation of these crystals *v. supra.*) These crystals lose $7H_2O$ over H_2SO_4 *in vacuo*, or by heating to 75°, and the eighth H_2O at a red heat; they dissolve in about 3 parts boiling water, and 20 parts water at 15°. The solution is attended with disappearance of heat $[BaO^2H^2.8H^2O, Aq] = -15{,}207$ (*Th.* 3, 263). Crystals of $BaO_2H_2.H_2O$ melt at 83°–85° (Veley, *C. J.* 49, 371). According to Bechmann (*J. pr.* [2] 26, 388 and 474) pure BaO is obtained by heating $BaO_2H_2.8H_2O$ in a stream of O.

Barium, iodide of. BaI_2. Mol. w. unknown, as compound has not been gasified. S.G. 4·92 (Filhol, *A. Ch.* [3] 21, 415). H.F. $[Ba, I^2, Aq] = 144{,}520$ (*Th.* 3, 266).

Formation and Preparation.—Similar to methods for $BaBr_2$ (*q. v.*): also by action of gaseous HI on BaO.

Properties and Reactions.—A white, non-deliquescent, solid; easily soluble in water or alcohol; not decomposed by heat in absence of air, in presence of air BaO is formed and I evolved; wholly decomposed by heating in O (Schulze, *J. pr.* [2] 21, 407); aqueous solution absorbs CO_2 from air.

Combinations.—1. With *water* to form $BaI_2.7H_2O$ (Croft, *J. pr.* 68, 402; Thomsen, *B.* 10, 1343; Werther, *J. pr.* 91, 331, says the crystals are $BaI_2.2H_2O$). This hydrate forms needle-shaped crystals which deliquesce, with partial separation of I, in moist air, and melt on heating; heated in absence of air BaI_2 remains, one H_2O is lost at 100°, $5H_2O$ at 125° and the seventh H_2O at 150°. Thomsen gives these data $[Ba, I^2, 7H^2O] = 151{,}370$; $[BaI^2.7H^2O, Aq] = -6{,}850$.—2. With *baryta* to form $BaO.BaI_2.5H_2O$ (= $BaIOH.2H_2O$) (Beckmann, *J. pr.* [2] 26, 388 and 474); this salt crystallises from a mixture of conc. solutions of its constituents, in the ratio $BaO:BaI_2$.

Barium iodide, hydrated, *v.* BARIUM, IODIDE OF, *Combinations*, No. 1.

Barium, oxides of. Ba forms two oxides, BaO and BaO_2; the former is produced by the action of dry air, or O, on Ba; BaO heated to about 450° combines with O and forms BaO_2, which is again reduced to BaO at a higher temperature, or by reducing the pressure at 450°. Dry BaO_2 is stable, but the presence of water brings about slow decomposition to $BaO_2H_2 + O$; Berthelot (*A. Ch.* [5] 14, 433; comp. *C. R.* 85, 880) gives these data $[BaO, O] = -6{,}050$; $[BaO^2, H^2O] = 2{,}760$ (giving $BaO_2H_2 + O$). BaO is a strongly basic oxide; BaO_2 evolves O (or H_2O_2) and forms the same salts as BaO when acted on by acids.

I. BARIUM MONOXIDE (*Baryta*) BaO. Mol. w. unknown as compound has not been gasified. S.G. 4·65 (Playfair a. Joule, *C. S. Mem.* 2, 84); S.G. crystals 5·722 (Brügelmann, *W.* 2, 466;

4, 277); 5·456 (Filhol, *A. Ch.* [3] 21, 415). H.F. $[Ba,O] = 124, 240$; $[Ba,O,Aq] = 158, 760$ (*Th.* 3, 266; values approximate only, as Ba used was not pure).

Scheele distinguished baryta from lime in 1774; Gahn recognised the presence of this earth in heavy spar; Bergmann called the earth *terra ponderosa*; Kirwan gave the name *baryta*; Davy, in 1808, proved it to be a metallic oxide.

Formation.—1. By the action of dry air on Ba.—2. By strongly heating $BaCO_3$, best with $\frac{1}{10}$–$\frac{1}{12}$th of carbon whereby CO is formed which does not again combine with the BaO.—3. By strongly heating $Ba.2NO_3$; Rammelsberg (*B.* 7, 542) says that an oxide with the composition Ba_3O_4 ($= 2BaO.BaO_2$) is thus produced; Brügelmann (*W.* 2, 466; 4, 277) obtained hexagonal crystals of BaO by this method.—3. By strongly heating $BaCl_2$, or $BaSO_4$, to white heat, in a current of steam.

Preparation.—1. By strongly heating $Ba(IO_3)_2$ in a porcelain crucible until all I is removed.—2. By heating dry $Ba.2NO_3$ in a capacious porcelain vessel (best a retort), gradually raising the temperature when the salt melts, again raising the temperature to full redness when the residue in the vessel re-solidifies; the heating must be continued until all nitrate is decomposed, but no longer, as on long-continued heating CO_2 is absorbed; the portions in contact with the porcelain take up a little SiO_2 and Al_2O_3.

Properties.—A grey-white powder, very poisonous; melts at white-heat; takes up H_2O and CO_2 from the air; dissolves in water to form a caustic alkaline solution (*v.* Barium, hydroxide of).

Reactions.—1. Reduced by heating with *potassium*.—2. Decomposed to Ba + O by *electrolysis*.—3. Heated in *chlorine*, $BaCl_2$ and O are formed.—4. Heated with *sulphur*, BaS and $BaSO_4$ are produced.—5. Heated in *carbon disulphide* vapour, the products are BaS along with $BaCO_3$.—6. Heated in *phosphorus vapour*, in presence of H, barium phosphide BaP_2 (*q. v.*) and $Ba_2P_2O_7$ are formed (Dumas, *A. Ch.* [2] 32, 364).—7. Heated with *arsenic vapour* barium arsenite (*q. v.* under Arsenites) is said to be produced.

Combinations.—1. Combines with *water* to form BaO_2H_2 (*q. v.*) with production of much heat, and increase of volume: $[BaO, H^2O] = 22,260$; $[BaO, 9H^2O] = 49,730$ (*Th.* 3, 266).—2. With *carbonic anhydride*, to form $BaCO_3$ (dry BaO has no action on CO_2; Scheibler, *B.* 19, 1973); with *sulphuric anhydride* to form $BaSO_4$; $[BaO, CO^2] = 62,220$; $[BaO, SO^3] = 110,590$ (*Th.* 3, 266).—3. Heated in *air* or *oxygen* to about 450°, forms BaO_2 (*q. v.*).—4. With *methylic* or *ethylic alcohol*, forms $BaO.2CH_4O$ or $BaO.2C_2H_6O$.

II. Barium dioxide. BaO_2. Mol. w. unknown. S.G. 4·96 (Playfair a. Joule, *C. S. Mem.* 3, 84). Discovered by Thenard (*A. Ch.* 8, 308).

Formation.—1. BaO, or a mixture of BaO_2H_2 and CaO or MgO, is heated in nearly dry air, or O, to dull redness in a glass or porcelain tube.

Preparation.—A mixture of 4 parts finely powdered $KClO_3$ and 1 part BaO is thrown little by little into a porcelain crucible heated just to redness; the KCl formed is dissolved out by cold water (Liebig a. Wöhler, *P.* 26, 172); the impure hydrated BaO_2 containing BaO (Berthelot, *A. Ch.* [5] 6, 207, says the residue is nearly $BaO.BaO_2$) is rubbed in a mortar with water, and added little by little to very dilute HClAq, but not in quantity sufficient to neutralise the acid; the solution (which contains H_2O_2) is filtered, made slightly alkaline by addition of dilute BaOAq, whereby alumina and iron oxide are ppd., the liquid is again filtered through linen, and an excess of BaOAq is added; lustrous plates of $BaO_2.8H_2O$ are ppd.: (the filtrate must contain H_2O_2, proved by the production of a blue colour in ether when shaken with ether after acidifying and adding dilute $K_2Cr_2O_7Aq$); the pp. is washed with cold water, pressed between filter paper, and placed over H_2SO_4 until all water is removed and BaO_2 remains (Berthelot, *A. Ch.* [2] 6, 207). Or, H_2O_2Aq is added to BaOAq, the pp. of $BaO_2.8H_2O$ is washed with cold water, pressed between filter paper, and heated in dry air free from CO_2 to 100°–120° (Schöne, *B.* 6, 1172).—2. Pure BaO is heated to low redness in a stream of O (Brodie, *T.* 1850. 775).

Properties.—A white powder, resembling MgO; insoluble in, and combines with, water; melts at full red heat with evolution of O.

Reactions.—1. Decomposed by *heat* to BaO and O; at slightly reduced pressures (750 to 730 mm.) decomposition begins at about 450°; at ordinary pressure at a higher temperature than this; if the BaO produced is allowed to cool to 450° in presence of O under reduced pressure BaO_2 is re-formed (Boussingault, *A. Ch.* [5] 19, 464).—2. Decomposed very slowly by cold, quickly by hot, *water*, forming $BaO_2H_2 + O$ $[BaO^2, H^2O] = 2,760$ (giving $BaO_2H_2 + O$, Berthelot, *A. Ch.* [5] 14, 433).—3. *Conc. sulphuric acid* forms $BaSO_4$, and evolves O at temperatures above 60°–70°, but O mixed with ozone at lower temperatures (Houzeau, *C. R.* 40, 949).—4. Heated in dry *carbonic anhydride*, $BaCO_3$ and O are produced. 5. Heated with *carbon monoxide*, or *sulphurous anhydride*, light and heat are produced, and $BaCO_3$, or $BaSO_4$, is formed (Wöhler, *A.* 78, 125).—6. Acts as a powerful oxidiser towards *carbon*, *phosphorus*, &c., &c. (comp. Slater, *J. pr.* 65, 253; and Brodie, *T.* 1862. 837).—7. With dilute *acids* forms salts of Ba, and H_2O_2 or O.

Combinations.—1. With *water*, combines to form $BaO_2.8H_2O$ (produced also by action of BaOAq on H_2O_2Aq; *v. Preparation*); prismatic dimetric crystals, which lose $8H_2O$ *in vacuo*, or by heating in absence of CO_2 to 100°–120°. Berthelot gives the formula $BaO_2.10H_2O$ to the hydrate (*A. Ch.* [5] 21, 157); he also describes another hydrate with $7H_2O$ (*l.c.* [5] 6, 207); he gives the data $[BaO^2, 10H^2O] = 9,100$ (*l.c.* [5] 14, 433).—2. With *hydrogen peroxide* forms very unstable, monoclinic, crystals, $BaO_2.H_2O_2$; produced by adding excess of H_2O_2Aq to BaOAq, or by adding NH_3Aq to the solution of a Ba salt mixed with H_2O_2 (Schöne, *A.* 192, 257).

Barium, oxysulphides of, *v.* Barium, sulphides of; monosulphide, *Reactions*.

Barium, phosphide of. Described as a grey mass, having the composition BaP_2, produced by passing H charged with P vapour

over hot BaO; decomposed by H_2O, giving PH_3 and $BaHPO_3$ (Dumas, *A. Ch.* 32, 364).

Barium, salts of. Salts produced by replacing H of acids by Ba; they form one series belonging to the form BaX_2 where $X = Cl$, &c., $\frac{O}{2}, \frac{SO_4}{2}, \frac{CO_3}{2}$, &c. As none of these salts has been gasified we do not know the molecular weight of any of them; the spec. heat of Ba is undetermined; the formulæ are, therefore, based on analogies between these salts and those of similar metals which form gasifiable compounds, especially Zn and Cd, and also on analogies between the salts of Ba and Ca, the atomic weight of the latter metal having been settled by the spec. heat method. Barium forms salts with most, if not all, the acids; very few basic salts are known, and those which have been prepared are generally salts of the weaker acids, *e.g.* boric, tungstic, molybdic, &c. The haloid salts are very stable; the carbonate, nitrate, iodate, chlorate, &c., are decomposed by heat; Ba salts of the oxyacids are reduced by heating with C, H, or CS_2. Most Ba salts are isomorphous with the corresponding salts of Ca and Sr; many with the corresponding salts of Pb. A few Ba salts are soluble in water; the greater number are slightly soluble only, or insoluble (*v.* BORATES, CARBONATES, PHOSPHATES, SULPHATES, &c., &c.).

Barium, selenide of. BaSe. Mol. w. unknown. White solid, changing in air, obtained by heating $BaSeO_4$ in H to dull redness (Fabre, *C. R.* 102, 1469).

Barium, selenocyanide of. $BaSe_2(CN)_2$(?). Prepared by Crookes (*J. pr.* 53, 161). Data very meagre.

Barium, silicofluoride of. BaS[illegible] *v.* BARIUM FLUORIDE OF, *Combinations*, No. 3.

Barium, sulphides and hydrosulphide (or sulphydrate) of. Three sulphides of Ba are known; a fourth probably exists in solution. The monosulphide BaS is obtained by heating BaO in a stream of H_2S; by heating BaS + 2S to 360°, the trisulphide BaS_3 is formed; by boiling BaSAq with 3S and crystallising, BaS_4 may be prepared; and if BaSAq is boiled with considerable excess of S the solution reacts as if it contained a pentasulphide BaS_5. Only one hydrosulphide or sulphydrate, BaS_2H_2, is known. The sulphides and the hydrosulphide are fairly stable compounds; they are soluble in, and partly decomposed by, water; they resemble the sulphides of the alkali metals in their reactions, [illegible]S_2H_2Aq reacts with As_2S_3 to form barium thio-arsenite $Ba_3As_2S_6$ (*q. v.*). Sabatier (*A. Ch.* [5] 22, 1) gives the thermal data:—[BaO, H^2S] = 22,100; [BaS, O^4] = 236,500; [BaS, Aq] = 7,000.

I. MONOSULPHIDE. BaS.

Formation.—1. BaO is heated in a stream of H_2S.—2. $BaSO_4$ is reduced by heating in H or coal gas.

Preparation.—1. A stream of CO_2 is passed through CS_2 and then over red-hot $BaCO_3$; CS_2 must be in excess as BaS is decomposed by CO_2; the product is freed from higher sulphides by heating in H (Schöne, *P.* 112, 193).—2. $BaO_2H_2.H_2O$ (prepared by heating $BaO_2H_2.8H_2O$ to 80° in H) is acted on by dry H_2S; the products are BaS and H_2O (Veley, *C. J.* 49, 369).—3. Crude BaS (which is the starting point in the preparation of many Ba compounds) is prepared by mixing 8 parts heavy spar with 2 parts wood charcoal and 1 part rye meal, all in fine powder, making into a stiff paste with water, rolling into small cylinders, drying, packing in a crucible in alternate layers with charcoal, and gradually heating to full redness (Liebig, *A.* 35, 115; *v.* also Grüneberg, *J. pr.* 60, 168; Buchholz, *Ar. Ph.* 36, 275; Kuczinsky, *D. P. J.* 135, 455).

Properties.—A white amorphous solid; soluble in water; exposed to sunlight and then placed in the dark, it gives off light; oxidised in moist air.

Reactions.—1. In *moist air* decomposes to $BaCO_3$ and BaS_2O_3 with evolution of H_2S.—2. *Heated in air* is slowly oxidised.—3. Heated in *steam*, $BaSO_4$ is formed and H evolved (Lauth, *C. C.* 1863. 880).—4. *Chlorine, bromine,* and *iodine,* decompose BaS, forming BaX_2 (X = Cl, Br, or I) and S.—5. Dilute *acids* form Ba salts and evolve H_2S.—6. *Water* brings about partial decomposition into BaS_2H_2, BaO_2H_2, polysulphides and oxysulphides of Ba (*v.* Veley, *C. J.* 49, 369). The action of water on crude BaS has been examined in detail by H. Rose (*P.* 55, 415). If hot water is added in quantity just sufficient for solution, the liquid gives a pp. of MnS, without evolution of H_2S, on addition of an aqueous solution of a neutral manganous salt; the solution, therefore, contains either BaS or hydroxide and hydrosulphide in the ratio $BaO_2H_2:BaS_2H_2$;

($?BaO_2H_2Aq + BaS_2H_2Aq + 2MnCl_2Aq = 2MnS + 2BaCl_2Aq + 2H_2O$). If cold water is added to crude BaS in an open vessel, in quantity rather less than sufficient for complete solution, and the liquid is evaporated, BaO_2H_2 separates out, then various oxysulphides (*v. infra*), then, on evaporating the mother liquor in a retort, crystals of $BaS.6H_2O$ (*v. infra, Combinations*) separate, and finally on evaporating to dryness BaS_2H_2 remains.

The *oxysulphides* prepared as above described, or by cooling the solution obtained by acting on crude BaS with boiling water in a closed vessel, seem to be three:

$Ba_7O_4S_3.58H_2O [= 4(BaO_2H_2.9H_2O).3(BaS.6H_2O)]$,
$Ba_2OS.10H_2O [= (BaO_2H_2.8H_2O)(BaS.H_2O)]$, and
$Ba_4S_3O.28H_2O [= (BaO_2H_2.9H_2O).3(BaS.6H_2O)]$.

The compositions of these bodies are, however, far from settled; the compounds are very unstable and are separated by recrystallisation into BaO_2H_2 and BaS_2H_2. If successive quantities of cold water, each less than sufficient for complete solution, are shaken with crude BaS in a closed vessel for some hours, the first solution contains BaS_2H_2 along with a little of the higher sulphides of Ba (the solution gives MnS and also H_2S on addition of $MnCl_2Aq$); the next solution contains either BaS or BaO_2H_2 and BaS_2H_2 in the ratio $BaO_2H_2:BaS_2H_2$ (with $MnCl_2$ it gives MnS without evolving H_2S); the following solutions contain BaO_2H_2, as they give more and more MnO_2H_2 on addition of $MnCl_2Aq$ and less and less MnS.

Combinations. — With *water* BaS forms $BaS.6H_2O$; prepared as above described, also by evaporating *in vacuo* a solution of BaS after addition of a little S (Schöne, *P.* 112, 193); or

by evaporating BaS_2Aq (q. v.) *in vacuo*. $BaS.6H_2O$ crystallises in white six-sided plates; slightly soluble in cold, easily in hot, water; insoluble in alcohol; loses $6H_2O$ between 100° and 350° with partial decomposition.

II. Trisulphide. BaS_3. Prepared by heating 2 parts BaS with 1 part S, and removing excess of S by distilling it off at 360° (Schöne, *P.* 112, 193). Forms a yellowish-green mass, soluble in hot water; heated to redness in absence of air gives BaS + 2S. A solution of BaS_3 in much boiling water evaporated *in vacuo* deposits (1) $BaS.6H_2O$ (*v. supra*), then (2) a mixture of $BaS_4.H_2O$ (*v. infra*) and orange dichroïc monoclinic prisms of $3(BaS.6H_2O).(BaS_4.H_2O).6H_2O$ (Schöne, *l.c.*).

III. Tetrasulphide. Known only in combination with H_2O as $BaS_4.H_2O$. By evaporating a solution of BaS_3 in hot water *in vacuo*, or by evaporating BaSAq with 3S, trimetric, dichroïc, needles separate; yellow by transmitted, red by reflected, light; soluble in water, may be recrystallised from hot water; insoluble in alcohol; at 300° lose H_2O with decomposition into H_2S, S, and BaS_3 (Schöne, *l.c.*). A more hydrated salt, probably $BaS_4.2H_2O$, was obtained by Veley by dissolving S in BaS_2H_2Aq (*C. J.* 49, 378).

IV. Pentasulphide. BaS_5. Not known in definite form. BaSAq or BaS_2H_2Aq boiled with excess of S, yields a yellow alkaline solution, from which on cooling S and BaS_4 separate out; the mother liquor contains Ba and S in ratio $Ba:S_5$, on evaporation crystals of S separate out, and BaS_4 remains in solution (Schöne, *l.c.* confirming older observations of Berzelius).

V. Hydrosulphide or Sulphydrate. BaS_2H_2.

Formation.—By action of H_2O on BaS (*v.* Monosulphide; *Reactions*, No. 6).

Preparation.—BaOAq (saturated at 100°) is saturated with H_2S at 60°–70°; the liquid is decanted in absence of air, and is cooled to about 10°; the crystals of $BaS_2H_2.4H_2O$ which separate are dried between paper out of contact with air, and then heated in a stream of H (*v.* Veley, *C. J.* 49, 369).

Properties and Reactions.—With $4H_2O$ forms white acicular crystals, which effloresce in air, and gradually absorb O, forming BaS_2O_3 and $BaSO_4$; these crystals are soluble in water but insoluble in alcohol; aqueous solution evolves H_2S when boiled; heated to redness out of contact with air, H_2S is removed and BaS remains (for details, *v.* Veley, *l.c.*). BaS_2H_2 is strongly basic in its reactions; *e.g.* with As_2S_3 it forms Ba thio-arsenite.

Barium, sulphocyanide of. $Ba(SCN)_2$. Obtained by decomposing $NH_4.SCNAq$ by BaOAq (*v.* sulphocyanides, under Cyanides).

Barium, thio-antimonate of. $Ba_3(SbS_4)_2$. Obtained by the action of $BaCl_2Aq$ on Na_3SbS_4Aq (compare thio-antimonates under Antimony, thio-acids of).

Barium, thio-arsenite of. $Ba_3As_2S_6$. Obtained by digesting BaS_2H_2Aq with As_2S_3; and **Barium thio-arsenates** $Ba_3(AsS_4)_2$ and $Ba(AsS_3)_2$, obtained by the action of H_2S on $BaHAsO_4Aq$ (*v.* thio-arsenites and thio-arsenates under Arsenic, thio-acids of).

M. M. P. M.

BARYTA. *Oxide of Barium, v.* Barium, oxides of.

BASE.—The characteristic reaction of an acid is that the whole, or a portion, of the hydrogen of an acid can be displaced by a metal, with production of a new body, called a salt, composed of the metal and the elements of the acid, excepting the displaced hydrogen (*v.* Acids). If the oxide of a metal reacts with an acid to form a salt, the hydrogen displaced from the acid combines with the oxygen of the oxide to form water; the products of the reaction are a salt and water. The salt is not characterised by the properties either of the acid, the metal, or the metallic oxide; it has been built upon the metal or metallic oxide by combining this with the acid. The name *base* was given by Rouelle in 1744 to those bodies which reacted with acids to form salts. The name has sometimes been applied to metals, as well as to oxides and hydroxides of metals; at other times it has been confined to compounds of metals with H and O; at all times the conception underlying the name has been that of a substance which, while chemically very unlike an acid, reacts with acids to form salts. The dual origin of a salt is implied in the statement that for its production there is required the interaction of an acid and a base. A definition of any one of the terms, *acid, base, salt,* implies a definition of the other two. The chemical reaction characteristic of bases, as the term is now used, is the production of salts by the mutual reaction of a base and an acid; in some cases water is also formed, in other cases the salt is the sole product. Typical reactions are as follows:

$K_2OAq +$ [illegible] $Aq = K_2SO_4Aq + H_2O$

$2KO$[illegible]$q + H_2SO_4Aq = K_2SO_4Aq + 2H_2O$

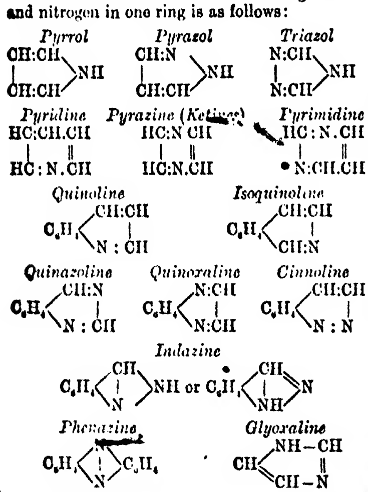
$2NH_3Aq + H_2SO_4Aq = (NH_4)_2SO_4Aq.$

A base may then be (i.) a metallic oxide, (ii.) a metallic hydroxide or an allied compound such as $NEt_4.OH$, $PMe_4.OH$, $SEt_3.OH$, &c., (iii.) ammonia or a derivative thereof, *e.g.* NH_2Et, NMe_3, &c. The terms *strong* and *weak* may be applied to bases with meanings similar to those given to the terms when applied to acids; a strong base, in this sense, is one which, when it reacts in aqueous solution with another base and an acid—all being present in equivalent quantities, and all possible products being soluble in water—combines with a large proportion of the acid and leaves only a small proportion for the other base to combine with. The hydroxides MOH, where M = an alkali metal or Tl, are strong bases; NH_3 is a weak base; [illegible] and NH_2Me are stronger bases than NH_3; NMe_4OH and SEt_3OH are nearly as strong bases as the alkalis (*v.* Affinity). By the term a *strong base* is sometimes meant a base which reacts with various acids to form very stable salts; *e.g.* salts which are not changed by water, hot or cold. In this meaning of the term BaO_2H_2 is a strong base, but BiO_3H_3 or SnO_2H_2 is a weak base. The oxides and hydroxides of polyvalent metals appear to be weaker bases than the corresponding compounds of the monovalent metals. The more positive a metal is, the more basic are its oxides and hydroxides. Sometimes a metallic oxide, or hydrated oxide, may react towards strong acids as a base, and towards strong bases as an acidic oxide; thus

$Al_2O_3.xH_2O$ reacts with H_2SO_4Aq to form $Al_2O_3.3SO_3$($=Al_2.3SO_4$), but $Al_2O_3.xH_2O$ reacts with much KOHAq to form $K_2O.Al_2O_3$ ($=K_2Al_2O_4$). In some cases the basic and acidic functions of a compound may be nearly equal; thus amido-acetic acid (? $CH_2.NH_2.COOH$) forms salts by its reactions with bases as other acids do, but it also combines with acids, as NH_3 does, to form salts. The hydroxides of certain metals which in some of their reactions behave as non-metals react as bases towards most acids, but if oxygen is added to these hydroxides compounds are formed which react as bases only towards the stronger acids and at the same time react as acids towards the stronger bases; such compounds are SnO_2H_2, and $SnO.O_2H_2$, respectively. Bases are sometimes divided into *mono-acid*, *di-acid*, *tri-acid*, &c., according as one reacting weight interacts with one, two, three, &c., reacting weights, of a monobasic acid, to form a salt. The poly-acid bases are weaker than the mono-acid bases. As examples of mono-acid bases may be given KOH, NH_3, NH_2Et, &c.; of di-acid bases, CaO_2H_2, BaO_2H_2, ZnO_2H_2, $NH_2C_2H_4$, &c.; of tri-acid bases, FeO_3H_3, $C_6H_3(NH_2)_2OH$, &c.; of tetra-acid bases, ZrO_4H_4, &c. (comp. ACIDS and SALTS). M. M. P. M.

BASES, ORGANIC, *v.* ALKALOIDS, AMINES, AMIDES, AZINES, PYRIDINE, QUINOLINE, &c.

The nomenclature of bases containing carbon and nitrogen in one ring is as follows:



BASIC OXIDES. Oxides which react with acids to produce salts. The greater number of the metallic oxides are basic; oxides of well-marked non-metals are never basic. The correlative term is *acidic oxides* (*v.* BASES, ACIDS, SALTS). M. M. P. M.

BASICITY OF ACIDS *v.* ACIDS, BASICITY OF.

BASILICUM, OIL OF. The essential oil obtained by distilling the leaves of Ocymum basilicum with water contains $C_{10}H_{16}3H_2O$ which crystallises in prisms (Dumas a. Peligot, *A.* 14, 75).

BASSIA LATIFOLIA. The seeds of this Himalayan plant yield by pressure a buttery substance, [illegible], containing olein and stearin (Hardwick, *C. J.* 2, 231).

BASSORIN. The insoluble gum acid, probably meta-arabic acid, or at least a meta- acid allied thereto (*v.* ARABIN) of gummi bassora, G. Toritonense, or G. Kutera. These gums consist of a part (the meta- acid) that swells up to a jelly when they are treated with water, and of a soluble part, the alkaline or earthy salt of the acid. C. O'S.

BASTOSE *v.* CELLULOSE.

BASYLOUS. A name sometimes applied to the more positive, usually oxygen-containing, radicles, or groups of atoms, which combine with more negative, or *chlorous*, groups to form salts; *e.g.* $\overset{+}{K_2O}.\overset{-}{SO_3}$, $\overset{+}{K_2O}.\overset{-}{CrO_3}$, $\overset{+}{Cr_2O_3}.\overset{-}{3SO_3}$, &c. The name is sometimes also applied to the elements which displace H from acids with formation of salts. The correlative term is *chlorous*. M. M. P. M.

BDELLIUM. A gum-resin (Johnston, *J. pr.* 26, 145).

BEBEERINE $C_{19}H_{21}NO_3$. *Bebirine.* [180°]. Occurs, together with a resin (sepirin) and an acid (bebiric acid) in the bark of the bebeeru tree of Demerara (Rodie; Maclagan, *A.* 48, 106; Maclagan a. Tilley, *P. M.* 27, 186; v. Planta, *A.* 77, 333). It is an amorphous powder, v. sl. sol. water, v. e. sol. alcohol, v. sol. ether.—$B'_2H_2PtCl_6$: orange amorphous pp. Buxine has been considered to be identical with bebeerine (Walz, *N. J. P.* 14, 15).

BEE'S WAX *v.* WAX.

BEHENIC ACID $C_{22}H_{44}O_2$. *Benic acid.* [76°]. Occurs as glyceride in oil of ben and in the fatty oil of black mustard seed. Needles, resembling stearic acid.—NaA'.—BaA'$_2$.—PbA'$_2$.—EtA' [49°] (Voelcker; Strecker, *A.* 64, 346).

BEHENOLIC ACID $C_{22}H_{40}O_2$. *Benolic acid.* [57·5°]. Formed by the action of alcoholic potash on di-bromo-behenic acid (Haussknecht, *A.* 143, 41). White needles (from alcohol); v. sol. alcohol and ether, insol. water. Not reduced by sodium-amalgam, but combines with Br_2, forming $C_{22}H_{40}Br_2O_2$ [47°], and with Br_4, forming $C_{22}H_{40}Br_4O_2$ [78°].

Salts.—MgA'$_2$ 3aq.—AgA'.—BaA'$_2$.

BELLADONNINE. An alkaloid occurring in the mother-liquor from which sulphate of atropine (*q. v.*) has been crystallised (Hübschmann, *Schweiz. Z. Pharm.* 1858, 123; Kraut, *A.* 148, 236; *B.* 13, 165; Ladenburg a. Routh, *B.* 17, 152; Merling, *B.* 17, 381). Amorphous, v. sl. sol. water, v. sol. alcohol, ether, and chloroform. It is but slightly attacked by boiling baryta-water, but is split up by alkalis into tropic acid and oxy-tropine $C_8H_{15}NO_2$. This would indicate that belladonnine is oxy-atropine $C_{17}H_{23}NO_4$ (L.). According to Merling, belladonnine is $C_{17}H_{21}NO_2$ and gives tropine, atropic acid, and iso-atropic acid when boiled with baryta-water. Salts: $B'_2H_2PtCl_6$.—B'HAuCl$_4$.

BEN, OIL OF. A fatty oil expressed from the fruits of *Moringa nux behen.* It contains glyceryl palmitate, stearate, oleate, and behenate (*v.* BEHENIC ACID).

BENIC ACID *v.* BEHENIC ACID.

BENYLENE $C_{15}H_{28}$ (223°-228°). S.G. $\frac{0}{0}$ ·911. Formed by the action of alcoholic potash on

...amylene bromide $C_{11}H_{22}Br_2$ (Bauer a. Verson, *A.* 147, 252).

BENZACOIN $C_{22}H_{22}N_2O$. [150°]. A neutral crystalline substance obtained by extracting with alcohol the product of the action of $ZnEt_2$ on phenyl-acetonitrile (Frankland a. Tompkins, *C. J.* 37, 569).

BENZAL- *v.* BENZYLIDENE-.

BENZALDEHYDE *v.* BENZOIC ALDEHYDE.

BENZALDOXIM $C_6H_5.CH:N.OH$. *Oxim of benzoic aldehyde.* (c. 220° with decomposition). Colourless oil, formed by the action of hydroxylamine on benzoic aldehyde (Petraczek, *B.* 15, 2785). Formed also by reducing benzamidoxim with sodium-amalgam (Tiemann a. Krüger, *B.* 17, 1692). By heating with HCl it is split up into hydroxylamine and benzaldehyde. Ac_2O converts it into benzonitrile (Lach, *B.* 17, 1571).

Sodium salt $C_7H_6:N(ONa)aq$: white easily soluble plates, formed by the action of sodium ethylate on benzaldoxim in alcoholic solution; gives characteristic pps. with the salts of the heavy metals.

Hydrochloride $C_7H_6:N(OH),HCl$: white glistening scales, rotates on water.

Methyl ether $C_7H_6:N(OMe)$: (191° uncorr.); colourless oil, lighter than water and slightly soluble; formed by the action of methyl iodide and sodium ethylate on benzaldoxim; by HCl it is split up into benzaldehyde and methyl-hydroxylamine.

Ethyl ether $C_7H_6:N(OEt)$: (208° uncorr.); colourless oil, split up by HCl into ethyl-hydroxylamine and benzaldehyde.

Propyl ether $C_7H_6:N(OC_3H_7)$: (225° uncorr.), colourless oil.

Iso-butyl ether $C_7H_6:N(OC_4H_9)$: (238° uncorr.), colourless oil.

Amyl ether $C_7H_6:N(OC_5H_{11})$: (161° uncorr.), colourless oil (Petraczek, *B.* 16, 823).

BENZAMIDE C_7H_7NO *i.e.* $C_6H_5.CO.NH_2$. *Amide of benzoic acid.* Mol. w. 121. [130°] (Ciamician a. Magnaghi, *B.* 18, 1828). S.G. 4 1·34 (Schröder, *B.* 12, 1612).

Formation.—1. From BzCl and NH_3.—2. Together with NH_4OBz, by the action of Bz_2O on NH_3.—3. From EtOBz and NH_3.—4. By boiling hippuric acid with water and PbO_2, or by heating hippuric acid in a current of dry HCl.

Properties.—Monoclinic tables: $a:b:c$ = ·228:1:1·068; β = 89° 22′ (Klein, *A.* 166, 184); v. sl. sol. cold water, m. sol. hot water, especially if it contain NH_3; v. sol. alcohol and ether.

Reactions.—1. It splits up into water and benzonitrile when heated with *dehydrating agents* (P_2O_5, P_2S_5, or H_2SO_4) and to some extent when heated alone at 290°.—2. *Boiling aqueous potash* forms KOBz.—3. *Boiling acids* form benzoic acid.—4. BzCl or Bz_2O form benzonitrile and benzoic acid.—5. Reduced in acid solution by *sodium-amalgam* to benzyl alcohol.—6. Boiling *phenol* gives benzoyl-phenol (PhOBz) and NH_3.—7. PCl_5 forms an unstable substance which rapidly splits up into HCl and benzonitrile (Wallach, *A.* 184, 19).—8. $COCl_2$ gives benzonitrile, cyaphenine, and di-benzoyl-urea (Schmidt, *J. pr.* [2] 5, 35).—9. $CSCl_2$ gives benzonitrile, COS, and HCl (Rathke a. Schäfer, *A.* 169, 107).—10. With *chloral* it combines forming $C_9H_8Cl_3NO$ [151°] (Wallach, *B.* 5, 251).—11. With *ethyl nitrite* it forms N_2, benzoic ether, and H_2O (Meyer a. Stüber, *B.* 4, 962).—12. Converted by *bromine in alkaline solution* into aniline (Hofmann, *B.* 18, 2737).—13. A solution of benzamide in *bromine* deposits crystals of unstable $BzNH_2Br_2$.

Combinations.—$BzNH_2HCl$: long prisms formed by saturating a mixture of benzamide and HClAq with HCl (Dessaignes, *A. Ch.* [3] 34, 146; Pinner a. Klein, *B.* 10, 1897). When exposed to the air it gives off all its HCl.—$BzNH_2\frac{1}{2}HCl$. [178°] (E. v. Meyer, *J. pr.* [2] 30, 122).

Salts.—$(BzNH)_2Hg$ [224°]. Formed by boiling benzamide with water and HgO. Laminæ (from alcohol); v. sol. alcohol and ether.—BzNHTl : slender needles (Church a. Crookes, *C. J.* 17, 151).

Additional References.—Liebig a. Wöhler, *A.* 3, 268; Fehling, *A.* 28, 48; Schwarz, *A.* 75, 195; Laurent, *Revue Scient.* 16, 391; Henry, *Z.* [2] 5, 446; Brauns, *Ar. Ph.* [2] 126, 214; Oppenheim a. Czarnomsky, *B.* 6, 1392; Guareschi, *G.* 4, 465; *A.* 171, 141; Kekulé, *B.* 6, 113; Schiff a. Tassinari, *B.* 10, 1785; Friedburg, *A.* 158, 26.

Benz-chloro-amide $C_6H_5.CO.NHCl$. Prepared by gradually adding a conc. solution of chloride of lime to a cold conc. solution of benzamide acidified with AcOH, the product being shaken out by ether as it is formed. Long colourless prisms (from water) (Bender, *B.* 19, 2274).

Dibenzamide $C_{14}H_{11}NO_2$ *i.e.* $NHBz_2$ [148°]. S. ·12 at 15°. Formed, together with benzamide, by the action of KNH_2 on BzCl dissolved in ether (Baumert a. Landolt, *A.* 111, 1); and from benzonitrile (10 g.) and fuming H_2SO_4 (7 g.) (Barth a. Senhofer, *B.* 9, 975; Gumpert, *J. pr.* [2] 30, 87). Trimetric crystals, $a:b:c$ = ·931:1:1·069. Sl. sol. boiling water, v. sol. alcohol, ether, and benzene.

Salts.—$NaNBz_2\frac{1}{2}aq$: small prisms, sol. ether.—$AgNBz_2$.

BENZAMIDINE $C_7H_8N_2$ *i.e.* $C_6H_5.C(NH).NH_2$ [75°-80°].

Preparation.—Benzonitrile is converted by treatment with isobutyl alcohol and HCl into the hydrochloride of $C_6H_5.C(NH).OC_4H_9$, whence ammonia produces benzamidine (Pinner a. Klein, *B.* 10, 1880; 11, 4).

Properties.—V. sol. water, sl. sol. ether, v. e. sol. alcohol; deliquescent; very volatile. Decomposed by heat into NH_3 and cyaphenine.

Salts.—B′HCl : flat needles.—$B'_2H_2PtCl_6$.—$AgC_7H_7N_2$.

BENZAMIDO- *v.* *Benzoyl*-AMIDO-.

BENZAMIDO-ACETIC ACID *v.* HIPPURIC ACID.

BENZ-AMIDOXIM $C_7H_8N_2O$ *i.e.* $PhC(NH_2).NOH$. *Benzenyl-oxamidine. Benzenyl-amidoxim. Isonitroso-benzylamine.* [80°].

Formation.—1. By the action of hydroxylamine on an alcoholic solution of benzonitrile (Tiemann, *B.* 17, 128).—2. By the action of hydroxylamine on the hydrochloride of benzamidine.—3. As a by-product in the action of hydroxylamine hydrochloride upon benzimido-ethyl-ether.—4. By digesting thio-benzamide with an alcoholic solution of hydroxylamine (Tiemann, *B.* 19, 1668). Long flat monosymmetrical prisms $a:b:c$ = 2·502:1:1·077. Volatilises

undecomposed. V. sol. alcohol, ether, benzene, and hot water, sl. sol. cold water. It is poisonous. It dissolves both in acids and alkalis. Fe_2Cl_6 gives a red colouration. The ammoniacal solution gives white crystalline pps. with $BaCl_2$, $AgNO_3$, $Pb(OAc)_2$, and $ZnSO_4$. The silver pp. on heating in the solution in which it is formed gives a splendid silver mirror.

Reactions.—1. Gives the carbamine reaction with *chloroform* and alcoholic *potash*.—2. *Nitrous acid* forms benzamide.—3. *Sodium amalgam* reduces it to benzaldoxim and NH_3 (Tiemann a. Nägeli, *B.* 18, 1086).—4. When quickly *heated* at 170° it splits up into benzonitrile and NH_3.—5. By heating with *acetic anhydride* it yields benzenyl-azoxim-ethenyl $C_6H_5.C\!\!<\!\!{}^{NO}_{N}\!\!>\!\!C.CH_3$.

Salts. A'Na: white crystalline solid, decomposed by water.—A'K: crystals.—A'Ag: unstable white crystalline pp. A'(CuOH): amorphous dark green pp.—A'H,HCl: large flat plates or concentric needles.—$A'H,H_2SO_4$: large prisms.—$(A'H)_2H_2SO_4$: amorphous solid.

Methyl ether.—A'Me: [57°]; (230° uncorr.); prisms; v. sol. alcohol, ether, and benzene, sl. sol. water. By HCl and $NaNO_2$ it is converted into benzenyl-methoxim chloride $C_6H_5.CCl(NOMe)$.

Ethyl ether.—A'Et: [67°]; trimetric plates. By dilute H_2SO_4 and sodium nitrite it is converted into benzhydroximic-ethyl-ether (*benzoyl-hydroxylamine ethyl ether*) $C_6H_5.C(OH)NOEt$. With HCl and $NaNO_2$ it yields benzenyl-ethoxim-chloride.

Benzyl ether. $A'C_7H_7$: [91°]; scales.

Benzoyl derivative. $C_6H_5.C(NH_2)$:NOBz: [140°]; slender white needles; v. sol. alcohol, ether, and aqueous acids, insol. water. On heating it readily splits off H_2O, giving rise to benzenyl-azoxim-benzenyl $C_6H_5.C\!\!<\!\!{}^{N.O}_{N}\!\!>\!\!C.C_6H_5$.

Acetyl derivative $C_6H_5.C(NH_2)$:NOAc. [96°]; thin plates or flat prisms, sol. alcohol, sl. sol. ether, v. sl. sol. water. By boiling with water it loses H_2O and is converted into benzenyl-azoxim-ethenyl.

Butyryl derivative $C_6H_5.C(NH_2)$:$NO.CO.C_3H_7$. [94°]: fine needles.

Ethylene ether $(Ph.C(NH_2):NO)_2C_2H_4$. [156°]. White plates. Sol. alcohol, ether, benzene, and ligroin, insol. water. Formed by heating an alcoholic solution of benz-amidoxim (2 mols.) and sodium ethylate (2 mols.) with ethylene bromide (1 mol.).

Compound with chloral $C_9H_9N_2Cl_3O_2$. [135°]. Obtained by mixing the constituents. White crystalline powder. V. sol. alcohol and ether, insol. water. By treatment with H_2SO_4 or by long boiling with water it is resolved into its components (Falck, *B.* 19, 1485).

References.—Pinner, *B.* 17, 184; Tiemann a. Krüger, *B.* 17, 1685; 18, 731, 1053; Tiemann, *B.* 19, 1479, 1668; Schulz, *B.* 18, 1080; Falck, *B.* 19, 1484 (*v.* also Azoxims).

Benz-amidoxim-carbonic ether $C_6H_5.C(NH_2)$:$N.O.CO_2Et$. [127°]. Formed by the action of chloroformic ether upon benz-amidoxim (Falck, *B.* 18, 2467). Long glistening needles. V. sol. alcohol, ether and benzene, less in ligroin. On heating it splits off alcohol, forming benzenyl-azoxim-carbinol $C_6H_5.C\!\!<\!\!{}^{N.O}_{N}\!\!>\!\!C(OH)$.

Carbonyl-di-benz-amidoxim $C_{15}H_{14}O_3N_4$, *i.e.* $\begin{matrix}C_6H_5.C(NH_2):NO\\C_6H_5.C(NH_2):NO\end{matrix}\!\!>\!\!CO$. [129°]. Formed by the action of carbonyl chloride upon benz-amidoxim dissolved in benzene (Falck, *B.* 18, 2470). White plates. Sol. alcohol and ether, v. sl. sol. benzene, insol. water.

BENZ-AMIDOXIM-*m*-CARBOXYLIC ACID $C_8H_8N_2O_3$ *i.e.* [3:1] $C_6H_4(CO_2H).C(NOH)NH_2$. [200°]. Crystalline solid. Sol. hot water and alcohol, sl. sol. ether, nearly insol. chloroform and benzene.

Formation.—1. By saponification of the ethyl ether which is obtained by combination of *m*-cyano-benzoic ether with hydroxylamine.—2. By digesting a mixture of equivalent quantities of *m*-cyano-benzoic acid, hydroxylamine hydrochloride, and sodium carbonate, in dilute alcoholic solution for 12 hours at 80°-100°.

Reactions.—The aqueous solution of the ammonium salt gives sparingly pps. with $CuSO_4$, $Pb(OAc)_2$, $AgNO_3$, and $ZnSO_4$. Heated with acetic anhydride it is converted into *m*-carboxy-benzenyl-azoxim-ethenyl $C_6H_4(CO_2H).C\!\!<\!\!{}^{N.O}_{N}\!\!>\!\!C.CH_3$.

Ethyl ether A'Et [118°]; needles; v. sol. alcohol, sl. sol. water (Müller, *B.* 19, 1495).

Benz-amidoxim-*p*-carboxylic acid [4:1] $C_6H_4(CO_2H).C(NOH)NH_2$ [above 330°]. Formed by digesting *p*-cyanobenzoic acid (1 mol.) hydroxylamine hydrochloride (1 mol.), and sodium carbonate (1 mol.) in dilute alcoholic solution for 18 hours. Sol. dilute alcohol, sl sol. water, nearly insol. absol. alcohol, ether, and benzene. A dilute aqueous solution of the ammonium salt gives pps. with $CuSO_4$ and with $AgNO_3$. By boiling with acetic anhydride it is converted into *p*-carboxy-benzenyl-azoxim-ethenyl $C_6H_4(CO_2H).C\!\!<\!\!{}^{N.O}_{N}\!\!>\!\!C.CH_3$ (Müller, *B.* 19, 1491).

Ethyl ether A'Et: [135°]; obtained by heating the ethyl ether of *p*-cyanobenzoic acid with hydroxylamine in alcoholic solution (Müller, *B.* 18, 2485). Colourless crystals; sol. boiling water.

BENZAM-MALONIC ACID *v.* Carboxy-phenyl-malonamic acid.

BENZAM-OXALIC ACID *v.* Carboxy-phenyl-oxamic acid.

BENZAM-SEBACIC ACID *v.* Carboxy-phenyl-sebacamic acid.

BENZAM-SUCCINIC ACID *v.* Carboxy-phenyl-succinamic acid.

BENZ-ANHYDRO- *v.* Benzenyl- or as derivatives of Benzamidine.

BENZARSEN- *v.* Arsenic, organic derivatives of.

BENZARSENIC ACID *v.* Arsenic, organic derivatives of.

BENZ-BROMO-QUINOLINE *v.* (*B.*)-Bromo-quinoline.

BENZ-CHLORO-AMIDE *v.* Benzamide.

BENZ-CHLORO-QUINOLINE *v.* (*B.*)-Chloro-quinoline.

BENZ-CREATIN

Benz-(α)-methyl-glycocyamine $NH_2.C(NH).NMe.C_6H_4.CO_2H$. From benzglycocyamine, conc. KOH, methyl alcohol, and MeI (Griess, *B.* 8, 324). Narrow laminæ (containing $1\frac{1}{2}$aq), sl. sol. water and alcohol. Decomposed by baryta into urea and methyl-amido-benzoic acid. – B'HCl aq. – $B'_2H_2PtCl_6$ 2aq.

Benz-(β)-methyl-glycocyamine $NHMe.C(NH).NH.C_6H_4.CO_2H$. From 'ethoxy-carbimidamido-benzoic acid' and cold conc. $NMeH_2$ solution. Laminæ, v. sl. sol. cold water. Boiling baryta forms methyl-urea and amido-benzoic acid. – B'HCl. – $B'_2H_2PtCl_6$ 2aq.

BENZCREATININE

o-**Benz-(α)-methyl-glycocyamidine** $C_9H_9N_3O$ *i.e.* $HN=C\left\langle\begin{array}{l}N(CH_3)-C_6H_4\\ \qquad\qquad\quad\ |\\ NH\text{——}CO\end{array}\right.$. Prepared by the action of MeI on *o*-benzglycocyamidine (Griess, *B.* 13, 978). White needles. Sol. alcohol, sl. sol. ether and hot water. Insol. caustic alkalis.

Salts. – B'HCl aq: soluble plates. $(B'HCl)_2PtCl_4$.

o-**Benz-(β)-methyl-glycocyamidine** $C_9H_9N_3O$ *i.e.* $HN=C\left\langle\begin{array}{l}NH\ -\ C_6H_4\\ \qquad\qquad\ |\\ N(CH_3)-CO\end{array}\right.$. Prepared by the action of methylamine on 'ethoxy-cyan-amido-benzoyl' $(C_{10}H_{10}N_2O_2)$ (Griess, *B.* 13, 978). White needles. Sol. caustic alkalis. Weak base.

Salts.—B'HCl: small tables or prisms, decomposed by water. – $(B'HCl)_2PtCl_4$: sparingly soluble yellow plates.

BENZCYANIDINE *v.* BENZOYL CYANIDE.

BENZEÏNS. These bodies, which much resemble the phthaleïns, are hydroxylated aromatic carbinols, such as di-oxy-tri-phenyl carbinol $C_6H_5.C(C_6H_4OH)_2(OH)$. Prepared by heating phenols with benzotrichloride. The compound from resorcin is yellow, those from cresols, pyrocatechin, hydroquinone, orcin, and (β)-naphthol are yellow or yellowish-red, pyrogallol gives a blue, and (α)-naphthol a green dye. On reduction they give the corresponding derivatives of methane (Doebner, *B.* 13, 610; *A.* 217, 227).

BENZENE C_6H_6. Mol. w. 78. [6°]. (80·1°) (R. Schiff, *A.* 220, 91). S.G. $\frac{15}{4}$ ·8839 (S.); $\frac{20}{4}$ ·8799 (Brühl). V.D. 2·74 (calc. 2·70) (S.). S.H. ·3834 + ·001043*t* at *t*° (R. Schiff, *A.* 234, 320). H.C.p. (liquid) 776,000 (Berthelot, *A. Ch.* [5] 23, 193); 779,530 (Stohmann, Rodatz a. Herzberg, *J. pr.* [2] 33, 258); (gaseous) 799,350 at 18° (*Th.*); 787,488 (S. R. a. H.). H.F.p. (as vapour) – 12,510 (Thomsen, *Th.* 4, 61); H.F.v. – 13,670 (*Th.*). C.E. (14·2 to 80·1) ·00136 (S.). S.V. 95·94 (S.); 95·8 (Ramsay, *C. J.* 35, 463). μ_β 1·5134 (B.); μ_D 1·5062 at 14° (Negreano, *C. R.* 104, 423); 1·5050 (Gladstone, *C. J.* [2] 7, 101). R_∞ 42·16 (B.); 44·02 (Kanonnikoff, *J. pr.* [2] 31, 352). *Dielectric constant* 2·292 at 14° (N.).

Formation.—1. By heating benzoic acid with lime (Mitscherlich, *A.* 9, 39; Peligot, *A.* 9, 48, 257; 11, 277; 12, 39), or by passing the vapour of benzoic acid over red-hot iron (Darcet, *A. Ch.* [2] 66, 99).—2. By heating phthalic acid with lime (Marignac, *A.* 42, 217). – 3. By dry distillation of quinic acid (Wöhler, *A.* 51, 146).—4. By passing oil of bergamot over red-hot lime (Ohme, *A.* 31, 318).—5. Together with naphthalene, styrene, retene, &c., by heating acetylene to a red heat (Berthelot, *A. Ch.* [4] 9, 469). Benzene is among the products obtained by passing toluene, xylene, ψ-cumene, or styrene through a red-hot tube.—6. Metallic succinates give on dry distillation a liquid (hydroquinone dihydride ?) which yields benzene when distilled with zinc-dust (v. Richter, *J. pr.* [2] 20, 206).—7. From benzene sulphonic acid by passing steam through its solution in diluted H_2SO_4 at 175° (Armstrong a. Miller, *C. J.* 45, 148).—8. From phenol (70 g.) by distilling with P_2S_5. The yield is small (16 g.): $8C_6H_5OH + P_2S_5 = 2(C_6H_5)_3PO_4 + 3H_2S + 2C_6H_6$ (A. Geuther, *A.* 221, 55).—9. The homologues of benzene when treated at their boiling-points with a current of HCl gas in presence of Al_2Cl_6 evolve MeCl and yield lower homologues, but at the same time part of the MeCl attacks other portions of the hydrocarbon with production of higher homologues. Thus if HCl is passed into boiling *m*-xylene containing Al_2Cl_6, benzene, toluene, pseudocumene, mesitylene, and durene are obtained (Jacobsen, *B.* 18, 338; Anschütz a. Immendorff, *B.* 18, 657).—10. Benzene is produced when benzylidene chloride, $PhCHCl_2$, or benzotrichloride, $PhCCl_3$ is heated with soda-lime (Limpricht, *A.* 139, 303).—11. From diazo-benzene nitrate or sulphate by heating with alcohol or alcoholic KOH.

Preparation.—1. Coal tar is distilled and the fraction boiling below 150° is freed from phenols by shaking with NaOHAq and from bases by shaking with H_2SO_4. It is then rectified. It is convenient to keep the still-head at 100°: toluene is then condensed while benzene passes over (Faraday, *T.* 1825, 440; Hofmann a. Mansfield, *C. J.* 1, 244). On the large scale the distillation is performed in an iron boiler, to which is attached a tall vertical column divided into compartments; the fire is regulated so that pure benzene passes over, while its homologues condense and run back to the boiler. Benzene is completely freed from its homologues by cooling with ice and salt, when it solidifies and the homologues which remain fluid may be pressed out. It is freed from thiophene by shaking with conc. H_2SO_4.—2. A mixture of benzoic acid (1 pt.) and slaked lime (3 pts.) is distilled from an iron tube: the product is shaken with KOHAq, distilled with steam, dried with $CaCl_2$ and Na and rectified. Diphenyl and benzophenone are by-products. The benzoic acid used must not be prepared from toluene, otherwise it will contain thiophenic acid, and the benzene will contain thiophene.

Properties.—Colourless, mobile, strongly refracting liquid. Volatile with steam. Scarcely soluble in water, v. e. sol. alcohol, ether, glacial acetic acid, acetone, and chloroform. Crystallises in trimetric pyramids, *a*:*b*:*c* = ·891:1:·779 (Groth, *Z.* [2] 6, 553). It dissolves S, P, I, fats, resins, oils, and many alkaloids. It burns with a luminous flame; 1g. burnt with excess of hydrogen giving out a light equal to 5·8 g. of spermaceti. When burnt with CO, and CH_4, the light equals that of 6·1 g., and 7·8 g., of spermaceti respectively (Frankland a. Thorne, *C. J.* 33, 93). There are four bands in the

ultra-violet absorption-spectrum of benzene (Hartley, *C. J.* 39, 163; 47, 694).

Detection.—Benzene is converted by fuming HNO_3 into nitro-benzene; this is washed with water and reduced by tin and HCl to aniline; caustic soda is added and the aniline extracted with ether; the ether is evaporated and the aniline dissolved in much water; the aqueous solution gives a violet colour with bleaching-powder. A mixture of HNO_3 and H_2SO_4 forms di-nitro-benzene, which, after crystallising from dilute alcohol, melts at 89°.

Detection of Thiophene in Benzene.—Thiophene, which is usually present in small quantities in commercial benzene, is indicated by the blue colour produced by shaking with conc. H_2SO_4 and isatin (V. Meyer, *B.* 16, 1465; Baeyer, *B.* 12, 1309).

Impurities.—Crude benzene may contain traces of toluene, xylene, thiophene, CS_2, amylene, crotonylene, alcohol, and acetonitrile.

Reactions.—1. Benzene when passed through *a red-hot tube* forms hydrogen, a little acetylene, diphenyl, benzerythrene $C_{24}H_{18}$, *p*-di-phenyl-benzene, iso-di-phenyl-benzene, and triphenylene (Berthelot, *Bl.* [2] 6, 272, 279; G. Schultz, *A.* 174, 201; H. Schmidt a. G. Schultz, *A.* 203, 118).—2. A mixture of benzene vapour and *ethylene* passed through a red-hot tube gives diphenyl and small quantities of anthracene, styrene, and phenanthrene (Berthelot, *Bl.* [2] 7, 113, 274; Ferko, *B.* 20, 660).—3. A mixture of equivalents of benzene and *toluene* dropped at the rate of 80 g. per hour from a tap funnel into the turned-up end of an iron tube kept at low red heat is converted, to the extent of about 10 per cent., into gases, naphthalene, diphenyl, *p*-tolyl-di-phenyl, *o*-*p*-di-tolyl, (γ) and (δ) di-phenylene-methane, phenanthrene, anthracene, *p*-di-phenyl-benzene, a hydrocarbon $C_{32}H_{28}$, a hydrocarbon [13°] (293°–316°) and two liquid hydrocarbons (359°–383°) and (404°–427°) (Carnelley, *C. J.* 37, 701).—4. *Induction sparks* passing through liquid benzene produce a gas that contains 42 p.c. acetylene and 57 p.c. hydrogen (Destrem, *Bl.* [2] 42, 267).—5. *Aluminium chloride* (*v.* p. 147) acting upon a mixture of benzene and an alkyl chloride causes HCl to escape with the resulting formation of an alkyl-benzene (Friedel a. Crafts, *C. R.* 84, 1392, 1450; 85, 74; *A. Ch.* [6] 1, 449). (*a*) Thus *methyl chloride* passed into a mixture of benzene and Al_2Cl_6 gives toluene, *o*-, *m*-, and *p*-xylene, ψ-cumene, mesitylene, durene, isodurene, penta-methyl-benzene, and hexa-methyl-benzene (Ador a. Rilliet, *B.* 12, 329; Jacobson, *B.* 14, 2624). (*b*) *Chloral* is converted by benzene in presence of Al_2Cl_6 into $CPhCl_2.CH(OH)Cl$, the hydrochloride of $\alpha\alpha$-di-chloro-phenyl-acetic aldehyde (Combes, *C. R.* 98, 678; *Bl.* [2] 41, 382). (*c*) *Methylene chloride* in presence of Al_2Cl_6 gives di-phenyl-methane, anthracene, and toluene (Friedel a. Crafts, *Bl.* [2] 41, 322). (*d*) *Chloropicrin*, Al_2Cl_6, and benzene form $CHPh_3$ and Ph_3COH (Elbs, *B.* 16, 1274). (*e*) *Allyl chloride*, Al_2Cl_6, and benzene give di-phenyl-propane and *n*-propyl-benzene (Wispek a. Zuber, *A.* 218, 374). (*f*) *Vinyl bromide*, Al_2Cl_6, and benzene give ethyl-benzene, *u*-di-phenyl-ethane, and di-methyl-anthracene dihydride (Angelbis a. Anschütz, *B.* 17, 167). *Vinyl tribromide*, $(CH_2Br.CHBr_2)$ gives di-phenyl... (*g*) *Oxygen* passed into boiling benzene containing Al_2Cl_6 forms phenol (Friedel a. Crafts, *C. R.* 86, 884; Senff, *A.* 220, 232). (*h*) *Sulphur* mixed with boiling benzene and Al_2Cl_6 forms phenyl mercaptan, di-phenyl sulphide and 'diphenylene disulphide' $(C_6H_4)_2S_2$ (Friedel a. Crafts, *C. R.* 86, 884). (*i*) *Sulphurous acid*, Al_2Cl_6, and benzene give di-phenyl-sulphoxide, Ph_2SO (Colby a. McLoughlin, *B.* 20, 195). (*j*) Acetylene in presence of Al_2Cl_6 forms styrene, di-phenyl-ethane and di-tolyls (Varet a. Vienne, *Bl.* [2] 47, 917).—6. Heated with Al_2Cl_6 (2 pts.) at 200° in sealed tubes benzene gives toluene, ethyl-benzene, and diphenyl (Friedel a. Crafts, *C. R.* 100, 692).—7. Phenol is among the products of *oxidation* of benzene by H_2O_2 (Leeds, *Ph.* [3] 11, 1068; *cf.* Kingzett, *C. N.* 44, 229). Phenol is also formed when benzene is digested for some days at 40° with cuprous chloride and dilute HCl, atmospheric oxygen attacking benzene and Cu_2Cl_2 simultaneously (Nencki a. Sieber, *J. pr.* [2] 26, 25). In the animal body it is oxidised to hydroquinone and pyrocatechin (Nencki a. Giacosa, *H.* 4, 325; *cf.* Schultzen a. Naunyn, *C. C.* 1867, 705). Oxidation with MnO_2 and dilute H_2SO_4 produces formic, benzoic, and phthalic acids (Carius, *Z.* 4, 505; *A.* 148, 50). The formation of benzoic acid is perhaps preceded by that of diphenyl (Kekulé). PbO_2 and H_2SO_4 give benzoic acid; PbO_2 and boiling dilute HNO_3 give only oxalic acid; CrO_3 gives only CO_2 (Holder, *Am.* 7, 114).—8. PCl_3 at a red heat forms $PhPCl_2$, diphenyl, and ... (Michaelis, *A.* 181, 265; Köhler, *B.* 13, 1623).—9. S_2Cl_2 at 250° forms chloro-benzene, HCl, and S (Schmidt, *B.* 11, 1168).—10. *Iodic acid* and H_2SO_4 on heating slowly form iodo-benzene (Peltzer, *A.* 136, 194).—11. SO_2Cl_2 at 150° gives chloro-benzene (Dubois, *Z.* [2] 2, 705).—12. $Cl.SO_2.OH$ forms $PhSO_2Ph$, $PhSO_2Cl$, and $PhSO_3H$ (Knapp, *Z.* [2] 5, 41).—13. HClO forms $C_6H_6(OH)_3Cl_3$, the trichlor hydrin of phenose (Carius, *A.* 136, 323).—14. Aqueous $HClO_3$ forms trichloro-phenomalic acid, chloro-benzene, and dichloro-quinone (Carius, *A.* 142, 129).—15. CrO_2Cl_2 acting upon benzene diluted with HOAc (1 vol.) gives trichloro-quinone (Carstanjen, *J. pr.* 107, 331). When benzene is heated with CrO_2Cl_2 there is formed a brown pp. of $C_6H_4(CrO_2Cl)_2$ which is converted into quinone by water (Étard, *A. Ch.* [5] 22, 269).—16. Condenses with sulphuric acid and aldehydes, XCHO to $XCHPh_2$. Thus *chloral* forms $CCl_3.CHPh_2$; *bromal* forms CBr_3CHPh_2; *chloro-aldehyde* forms $CH_2Cl.CHPh_2$; formic aldehyde forms CH_2Ph_2 (Goldschmiedt, *B.* 6, 985; Hepp, *B.* 6, 1439).—17. Benzene is not attacked by HIAq and P at 250°, but at 280° it gives hexahydro-benzene (Wreden a. Znatowicz, *A.* 187, 163; *cf.* Berthelot, *A. Ch.* [3] 15, 150).—18. When *chlorine* is passed into benzene containing thiophene HCl is evolved and the benzene then no longer gives the indophenine reaction (Willgerodt, *J. pr.* [2] 33, 480). Pure benzene is not attacked by chlorine in the cold and in the dark, but at 80° or in sunlight benzene hexachloride is formed. In presence of carriers, *i.e.* substances capable of combining with chlorine in more than one proportion, chloro-benzenes are produced.—19. *Nitric acid* forms nitro- and di-nitro-benzene.

[illegible] —$(C_6H_6)_2AlCl_3$ [illegible]. Decomposed by water into benzene and alumina; with Br it gives C_6Br_6 (Gustavson, *B.* 11, 2151).—$(C_6H_6)_2AlBr_6$.—$(C_6H_6)_2 3SbCl_3$: monoclinic tables, formed by warming $SbCl_3$ with benzene (Watson Smith a. Davis, *C. J.* 41, 411).

Potassium-benzene C_6H_5K mixed with $C_6H_4K_2$. Formed by heating benzene with K at 250° (Abeljanz, *B.* 5, 1027; 9, 10). Blue-black crystalline mass, insol. benzene. Takes fire in air. Converted by water into di-phenyl-benzene, hydrogen, and di-phenyl.

Constitution of Benzene.—That the molecular formula of benzene is C_6H_6, and not any multiple or submultiple of this, is settled, not only by its vapour density, but also by the existence of the following series: C_6H_5Cl, $C_6H_4Cl_2$, $C_6H_3Cl_3$, $C_6H_2Cl_4$, C_6HCl_5, C_6Cl_6. We may call the six atoms of hydrogen in the molecule of benzene, *a, b, c, d, e, f*. The first question is: are these six atoms of equal value, or could we, by displacing *a* by an element or radicle R, get a product different from that which would be produced by displacing *b* by R?

Proposition I.—*Four, at least, of the hydrogen atoms are of equal value.*

Ordinary phenol contains hydroxyl in place of one hydrogen: call this hydrogen *a*. Bromine and phosphorus convert phenol into C_6H_5Br. Sodium and carbonic acid convert this bromophenol into sodic benzoate, $C_6H_5.CO_2Na$. Hence the carboxyl of benzoic acid has taken the place of the hydrogen atom *a*. Now, there exist three *oxy*-benzoic acids, $C_6H_4(OH)(CO_2H)$, and since in these the carboxyl is in position *a*, the three hydroxyls must have displaced three other atoms of hydrogen, say *b, c*, and *d*. When distilled with lime, these three acids, instead of giving three phenols, the hydroxyl being in places *b, c, d*, give the same phenol which is identical with the original phenol. Hence, the four hydrogen atoms which we have called *a, b, c*, and *d*, are of equal value (Ladenburg, *B.* 7, 1684).

Proposition II.—*To every hydrogen atom in the molecule of benzene there are two pairs of hydrogen atoms similarly related.* Benzoic acid, $C_6H_5(\overset{a}{CO_2H})$ gives bromo-benzoic acid, which we may call $C_6H_4\overset{c}{Br}(\overset{a}{CO_2H})$. This, when acted upon by nitric acid, produces *two* isomeric nitrobromo-benzoic acids. We may call these

$$C_6H_3(\overset{b}{NO_2})\overset{c}{Br}(\overset{a}{CO_2H}),\ \text{and}$$
$$C_6H_3(\overset{f}{NO_2})\overset{c}{Br}(\overset{a}{CO_2H}).$$

But by reduction these lose their bromine, and give rise to amido-benzoic acids:

$C_6H_4(\overset{b}{NH_2})(\overset{a}{CO_2H})$, $C_6H_4(\overset{f}{NH_2})(\overset{a}{CO_2H})$. These are found to be identical, being anthranilic acid. Hence, *b* and *f* are symmetrically related with regard to *a* (Hübner a. Petermann, *A.* 149, 129). Again, ordinary nitro-benzoic acid may be converted into the above bromo-benzoic acid by the diazo- reaction, hence it is $C_6H_4(\overset{c}{NO_2})(\overset{a}{CO_2H})$. On nitration it gives a di-nitro-benzoic acid which we may call $C_6H_3(\overset{c}{NO_2})(\overset{e}{NO_2})(\overset{a}{CO_2H})$, which may be reduced to $C_6H_3(\overset{c}{NO_2})(\overset{e}{NH_2})(\overset{a}{CO_2H})$, whence we may successively prepare $C_6H_3(\overset{c}{NO_2})\overset{e}{Cl}(\overset{a}{CO_2H})$, $C_6H_3(\overset{c}{NH_2})\overset{e}{Cl}(\overset{a}{CO_2H})$, and $C_6H_4\overset{e}{Cl}(\overset{a}{CO_2H})$. The last acid is found to be identical with the chloro-benzoic acid $C_6H_4\overset{c}{Cl}(\overset{a}{CO_2H})$ obtained by the diazo- reaction from $C_6H_4(\overset{c}{NO_2})(\overset{a}{CO_2H})$. Hence *c* and *e* are similarly related with regard to *a*. Therefore we have a second pair of hydrogen atoms similarly related with regard to *a* (Hübner, *A.* 222, 94, *cf.* Wroblewsky, *A.* 192, 206).

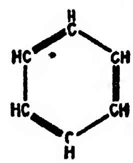
Proposition III.—*The six atoms of hydrogen in the molecule of benzene are of equal value.* Since *a, b, c*, and *d* are of equal value, and the situations of *f* and *e* are similar to those of *b* and *c* respectively, all six atoms of hydrogen are similarly placed and of equal value. This conclusion might also be deduced from the fact that no instance of isomerism among the mono-substitution products of benzene has been proved.

Isomerism among di-substitution products. Since two pairs of hydrogen atoms are symmetrical to any fifth, it follows, that only three di-derivatives of benzene can exist with a given formula. Using our former notation, these are—

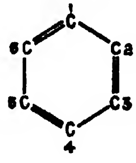
ab = *af*, *ac* = *ae*, and *ad*.

This is confirmed by experiment.

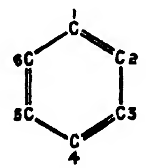
Structural formula.—Since the atom of carbon is assumed to be tetravalent, all the hydrogen atoms of benzene cannot be attached to the same atom of carbon, and symmetry requires that they must be either each attached to one carbon, or else three must be attached to one, and three to another; or, finally, two must be attached to one carbon, two to another, and the remaining two to a third. The two latter hypotheses do not account for more than two di-substitution products; hence the former is established. The carbon atoms must be united amongst themselves in a symmetrical fashion. Each atom of carbon must be united with at least two other atoms, or the group would not hold together; but it may be united with three other atoms. The former hypothesis results in the formula:



This is the ring-formula of Kekulé, which is one of the two formulæ originally put forward by him (*A.* 137, 160). If we number the positions occupied by the atoms of hydrogen thus,



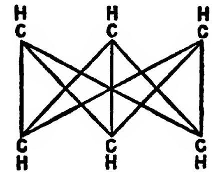
we see that the formula shows the possible existence of *four* di-substitution products—viz. 1:4, 1:3, 1:2 and 1:6. To get over this difficulty, Kekulé resorts to a peculiar mechanical hypothesis. He supposes that what we represent by straight lines in a formula really indicates that two atoms vibrate with reference to each other so that the above formula would mean that, in a given unit of time, 1 approaches 6 twice as often as it approaches 2; and so for the other atoms. Now, if this were the case, the di-substitution product 1:2 would differ from 1:6; but he assumes that the motions of 1 are as follows: first, it approaches 6 twice; then it approaches 2 once; next it approaches 6 *once*; then it approaches 2 *twice*; then 6 twice; 2 once; and so on. This is equivalent to saying that the above formula for benzene is true for one instant, after which it changes to



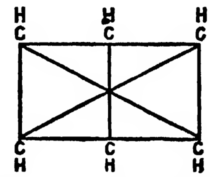
and the next instant it changes back again, and so on. This assumption leads to the deduction that only three di-derivatives can exist, and, if we could devise no other formula for benzene, we should be obliged to accept it. As a matter of fact, it is now almost universally adopted; not so much on its intrinsic merits, as on account of the enormous service which it has rendered to chemistry.

There remains, however, a second hypothesis possible, which is that every atom of carbon is united to three other atoms. The following mechanical construction may help to elucidate this hypothesis.

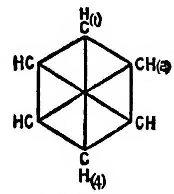
Let three rods be driven into the ground at the angles of an equilateral triangle, and let the top of each rod be joined by elastic string with the bottom of each of the two adjacent rods. A figure somewhat resembling a coronet is obtained, and we may suppose the six atoms of carbon in the benzene molecule situated at the two extremities of each of the three rods. At first sight it might appear that this representation of the benzene molecule would indicate the existence of three di-derivatives—namely, (1) when the substituted hydrogens are attached to two carbon atoms at opposite ends of one rod; (2) when they are attached to carbon atoms which are both on the upper or both on the lower ends of two different rods; (3) when one carbon atom is on the upper end of one rod and the other is on the lower end of another rod. But if we assume that formulæ and other mechanical symbols represent not actual position in space, but merely modes of combination of atoms, especially showing which atoms are directly and which indirectly united, (3) is identical with (1), for it can be converted into (1) by simply holding the string, at the opposite ends of which the carbon atoms have been placed, upright, and doing the same with the two corresponding strings. The rods will now take positions formerly occupied by the strings now held upright, and the figure will be the same as before. Hence this figure for benzene gives only two di-derivations, and accordingly it must be discarded. When the figure we have just considered is projected on a plane it assumes the form:



This figure, by simply twisting the central rod, is converted into



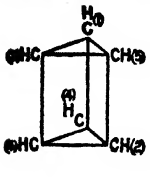
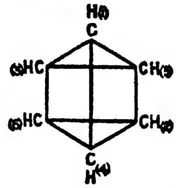
and if the central rod be now elongated we get:



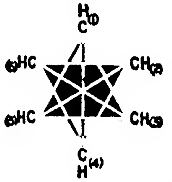
This symbol, which has been a favourite with some chemists, must, of course, be abandoned along with the solid figure from which it is derived; but it is also very easy to see that 1:2 and 1:4 di-derivatives, are identical, since if we pick up the carbon atom (4) and place it upon (2), and then take up (2) and place it where (4) was, supposing all the while that the connections, which we may imagine to be elastic, are not broken, the figure will be wholly unaltered.

There remains one other benzene formula: it is obtained by joining the ends of the three rods placed vertically by six strings as before, but with this difference, that whereas in the previous formula the top of one rod is joined to the bottom of the others, in this formula the top of each rod is joined with the top of each of the others, and the bottom of each rod is joined with the bottom of each of the others. We thus obtain a right-angled prism on a triangular base. This formula, defended by Ladenburg (*Theorie der aromatischen Verbindungen*, Brunswick, 1876), is capable of explaining most of the reactions of benzene, and the objections that have been brought against it are chiefly the

result of misconception of its nature. Projected upon a plane this formula becomes:

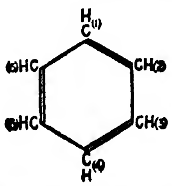



If the upper triangle be rotated through 180°, and then the figure be projected upon a horizontal plane, we obtain a figure which resembles **a star**:

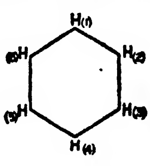


The two former figures are not symmetrical, but the latter is clearly so, and it has this advantage over the prism formula, that, if the atoms of carbon are numbered consecutively, they correspond to the atoms of carbon in Kekulé's formula, also numbered consecutively; whereas this would not be the case with the second of the three formulæ here given, which is that used by Ladenburg.

For most purposes it will not be necessary to decide which formula we adopt, for both the star-formula and the formula of Kekulé:



may be represented by the simple hexagon:



The numbering of the carbon atoms here given is used throughout this dictionary. Thus, the expression $C_6H_4Br_2$ [1:5] must be taken to mean that one bromine atom has displaced the hydrogen atom numbered (1) and the other the hydrogen atom numbered (5).

Physicists have tried to decide between the formulæ of Kekulé and Ladenburg. Thomsen (Th. iv. 272; A. 205, 133) considers that thermochemical data favour Ladenburg's formula, but the assumptions he makes in the course of his argument lead him in other cases to impossible conclusions. The specific volume of benzene is 96; whereas that calculated on the assumption that the S.V. of C = 11, and that of H = 5·5 is 99: this would merely show that the relation between the carbon atoms in the benzene molecule is different from that in saturated paraffins. If we compare the specific volumes of hexane, diallyl, and benzene, we find that:

Hexane, C_6H_{14} has a S.V. 140·0
Diallyl, C_6H_{10} „ „ 125·7
Benzene, C_6H_6 „ „ 95·9.

We see that the difference between the first and second (14·3) is less than that between the second and third (29·8) and that when hexane is converted into benzene by the removal of 8H the S.V. is lowered by 8 × 5·5, while the removal of 4H, in converting hexane into diallyl, lowers S.V. by only 4 × 3·6. That is to say the want of saturation of diallyl is accompanied by an unusually large specific volume, whereas this is not observed in the case of benzene. This would indicate that benzene is not unsaturated in the ordinary sense, and can be used as an argument in favour of Ladenburg's formula for benzene (Lossen, *A.* 214, 129; R. Schiff, *A.* 220, 303).

On the other hand, the S.V. of hexahydrotoluene (141·8) differs from that of toluene (118) by 23·8. This is about three times the difference (7·2) between the S.V. of pentane (117·2) and amylene (110). Hence it would appear that the change in the state of saturation in passing from hexahydrotoluene to toluene is of a similar character to the change in passing from pentane to amylene: the removal of H_2 in both cases producing a diminution of between 7 and 8 units in the S.V. This supports Kekulé's formula for benzene (Lossen, *A.* 225, 119; Horstmann, *B.* 20, 766).

The refractive power of benzene is about equal to that calculated on the assumption that Kekulé's formula is correct, provided that certain assumptions are made regarding the connection between the refractive powers of compound molecules and the refractive powers of the constituent atoms (Brühl, *A.* 200, 228; Kanonnikoff, *J. R.* 15, 473).

Passing from physical to chemical considerations, we note first that the behaviour of benzene towards halogens is, on the whole, more like that of a saturated than an unsaturated compound. The following special arguments have also been employed. Sodium acting upon succinic ether gives succinyl-succinic ether, which loses H_2 on oxidation, changing to di-oxy-terephthalic ether. The formula of succinyl-succinic ether may be written in one of the following ways:

(I.) $CO_2Et.CH.CO.CH_2$
$\quad\quad | \quad\quad\quad |$
$\quad CH_2.CO.CH.CO_2Et$

(II.) $CO_2Et.CH.C(OH){:}CH$
$\quad\quad | \quad\quad\quad |$
$\quad CH_2.C(OH){:}C.CO_2Et$

(III.) $CO_2Et.CH.C(OH){:}CH$
$\quad\quad | \quad\quad\quad |$
$\quad CH{:}C(OH).CH.CO_2Et$

(IV.) $CO_2Et.C : C(OH).CH_2$
$\qquad\qquad\quad | \qquad\qquad |$
$\qquad\qquad CH_2.C(OH):C.CO_2Et.$

(V.) $CO_2Et.CH.CO—CH_2$
$\qquad\quad | \qquad\qquad |$
$\qquad CO_2Et.CH.CO \;.\; CH_2.$

If the first correctly represents succinyl-succinic ether, it must be supposed to change into (II.), (III.), or (IV.) during the oxidation. The third formula would naturally lead to the formula

$$CO_2Et.C\begin{array}{c}\diagup C(OH)=CH \diagdown \\ \hline \diagdown CH=C(OH) \diagup\end{array}C.CO_2Et$$ and therefore

to the benzene formula $$HC\begin{array}{c}\diagup CH=CH \diagdown \\ \hline \diagdown CH=CH \diagup\end{array}CH$$

proposed by Wislicenus, a formula which would indicate the existence of two chloro-benzenes. The second formula

$$CO_2Et.CH\Big\langle\begin{array}{l}C(OH)=CH \\ CH_2-C(OH)\end{array}\Big\rangle C.CO_2Et,$$ would give

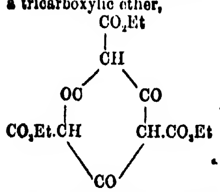
$$CO_2Et.C\Big\langle\begin{array}{l}C(OH)=CH \\ CH-C(OH)\end{array}\Big\rangle C.CO_2Et$$ on oxidation,

a formula based upon Kekulé's ring. The fourth formula, like the third, leads to the benzene ring of Wislicenus. The fifth formula would lead to Kekulé's or Wislicenus' ring, but with the carboxyls in the *ortho-* position, whereas in terephthalic acid they are in the *para-* position. Ladenburg's formula for dioxy-terephthalic acid is

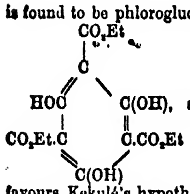
$$CO_2Et.C\begin{array}{c}\diagup CH\text{———}CH \diagdown \\ \text{—}|\text{———}|\text{ ——} \\ \diagdown C(OH)-C(OH) \diagup\end{array}C.CO_2Et,$$

the formation of which from formulæ I., II., III. or IV. requires the improbable assumption of a wandering of hydroxyl such as takes place when salicylic acid changes to *p*-oxy-benzoic acid. Ladenburg's formula can be derived from V, but only by assuming a rearrangement of the unsaturated unions.

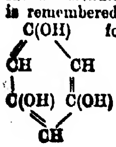
By the action of sodium upon malonic ether a tricarboxylic ether,



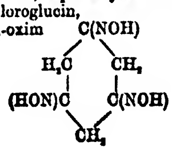
, is formed. This is found to be phloroglucin tri-carboxylic ether,



and this undoubtedly favours Kekulé's hypothesis, especially when it is remembered that phloroglucin,



forms a tri-oxim



as will soon be seen that, in spite of the great number of researches carried out on the benzene derivatives, the constitution of benzene itself still remains unsettled.

Recent discussions on the Benzene formula.—Ladenburg, *B.* 19, 971; 20, 62; Baeyer, *B.* 19, 1797; A. K. Miller, *C. J.* 51, 208; Thomsen, *B.* 19, 2944; Claus, *B.* 20, 1422.

Orientation.

Benzene gives rise to only one mono- substitution product. It gives three di- substitution products, and these, assuming either Kekulé's or Ladenburg's formula, are named as follows:

1, 2	=	1, 6	is called *ortho.*
1, 3	=	1, 5	„ „ *meta.*
1, 4			„ „ *para.*

When we come to tri- substitution products we must distinguish several cases.—1. Compounds of the formula $C_6H_3A_3$, that is to say, where the three substituting elements or radicles are all alike. There are three such compounds.

1, 2, 3	is called *consecutive.*
1, 3, 5	„ „ *symmetrical.*
1, 2, 4	„ „ *irregular.*

2. Compounds of the formula $C_6H_3AB_2$. There are six such compounds.—3. There are ten compounds of the formula C_6H_3ABC.

In the case of tetra- derivatives of benzene: 1. There are three compounds of the formula $C_6H_2A_4$:

1, 2, 3, 4	is called *consecutive.*
1, 2, 4, 5	„ „ *symmetrical.*
1, 2, 3, 5	„ „ *irregular.*

2. There are seven compounds of the formula $C_6H_2AB_3$.—3. There are thirteen compounds of the formula $C_6H_2A_2B_2$.—4. There are sixteen compounds of the formula $C_6H_2ABC_2$.—5. There are thirty compounds of the formula C_6H_2ABCD.

There is only one penta- derivative of the formula C_6HA_5, and only one compound of the formula C_6A_6.

The next question is how to determine, in a given case, the position of substituting radicles in the benzene ring. In isolated cases it is frequently found that this may be settled by special considerations, but the only general method known is that which was thoroughly worked out, by Kekulé's pupil Körner, in a most laborious research, in the course of which he discovered no less than 126 new compounds (*G.* 4, 305). This research has done more than anything else towards establishing the ring formula for benzene.

Suppose we convert $C_6H_4Br_2$ into $C_6H_3Br_3$; by reference to a figure it will be found that we can introduce a bromine atom in place of an atom of hydrogen in *ortho*-dibromobenzene in such a way as to produce either a consecutive or an irregular tribromobenzene, but not so as to produce a symmetrical product.

Meta-dibromobenzene can give rise to consecutive, irregular, or symmetrical, tribromobenzene, while *para*-dibromobenzene can only give rise to an irregular tribromobenzene.

An unknown dibromobenzene is therefore para-, ortho- or meta-, according as we can get one, two, or three tribromobenzenes by treating it with bromine. Thus the dibromobenzene from dibromoaniline gives rise to three tribromo-

benzenes; therefore it is a meta- compound. Again, the chief product of the action of two molecules of bromine upon benzene gives rise to only one tribromobenzene on further treatment with bromine; hence this product is para-dibromobenzene. On the other hand, the minor product of the dibromination of benzene gives rise to two, and only two, tribromobenzenes; therefore it is ortho-dibromobenzene.

In order to investigate the constitution of a given tribromobenzene, two methods may be followed: either introduce another atom of bromine in place of hydrogen and see how many tetrabromobenzenes result, or displace an atom of bromine by hydrogen and carefully examine how many dibromobenzenes are formed. It can easily be seen by reference to the formula that consecutive tribromobenzene produces two dibromobenzenes and also two tetrabromobenzenes, while symmetrical tribromobenzene produces one dibromo- and one tetrabromo- benzene, and irregular tribromobenzene gives rise to all three dibromobenzenes and all three tetrabromobenzenes.

The following are the melting and boiling points of the bodies described:

Dibromobenzenes.

Ortho	[−1°] (224°)
Meta	liquid (220°)
Para	[89°] (219°)

Tribromobenzenes.

Consecutive . . .	[87°]
Symmetrical . .	[120°] (278°)
Irregular . . .	[44°] (276°)

Tetrabromobenzenes.

Consecutive (1, 2, 3, 4)	[160°]
Symmetrical (1, 2, 4, 5)	[137°–140°]
Irregular (1, 2, 3, 5) am.	[99°] (329)

It will be observed that the isomerides differ widely in melting-points, but very slightly in boiling-points, and this is usually the case where isomerism is due to difference of position of substituents in the benzene nucleus.

The orientation of any given benzene derivative must be determined either by preparing it from one of the three bromobenzenes, or else by preparing a bromobenzene from it.

Examples.

Para-dibromobenzene when treated with sodium and methyl iodide gives a dimethylbenzene or xylene: $C_6H_4Br_2 + 2CH_3I + 4Na = 2NaI + 2NaBr + C_6H_4(CH_3)_2$. By oxidation this is converted first into toluic acid, $C_6H_4(CH_3)CO_2H$, and next into terephthalic acid, $C_6H_4(CO_2H)_2$. It is therefore evident that the xylene, the toluic acid, and terephthalic acid, are all *para*-compounds. Also since a certain bromotoluene, $C_6H_4Br(CH_3)$, when treated with sodium and methyl iodide gives the above *para*-xylene, it must be the *para*-bromotoluene, and the bromobenzoic acid derived from it by oxidation—$C_6H_4BrCH_3 + O_3 = C_6H_4Br.CO_2H + H_2O$—must be *para*-bromobenzoic acid.

As another example we may take the ortho-series. A certain bromoaniline, $C_6H_4Br.NH_2$, is known to be *ortho*- because when the amidogen is displaced by bromine the product is ortho-dibromobenzene. Now, this *ortho*-bromoaniline may be got by reducing a bromonitrobenzene $C_6H_4Br(NO_2)$, which may be formed by diazo-reaction from a nitroaniline $C_6H_4(NH_2)(NO_2)$, and this may be got by acting on a nitroanisol $C_6H_4(OCH_3)(NO_2)$ by ammonia, and this nitroanisol may be obtained from a nitrophenol $C_6H_4(OH)(NO_2)$, and this nitrophenol may be itself reduced to an amidophenol $C_6H_4(OH)(NH_2)$, and this amidophenol may be converted by diazo- reaction into a chlorophenol $C_6H_4(OH)Cl$, and this chlorophenol may be converted by cautious fusion with potash into a dioxybenzene $C_6H_4(OH)_2$. All the compounds here enumerated are clearly ortho- compounds, and as the dioxybenzene is found to be pyrocatechin, we have proved that *pyrocatechin* is *ortho*-dioxybenzene.

In the *para*- series we may trace, in the same way, the connection between *p*-dibromobenzene and *p*-nitroanisol $C_6H_4(OCH_3)NO_2$. Thence we proceed by the following steps: reduce to $C_6H_4(OCH_3)(NH_2)$, convert this into $C_6H_4(OCH_3)(OH)$ by nitrous acid, and treat with hydric iodide. In this way we get a second dioxybenzene, which is found to be *hydroquinone*, and this body is therefore a *para*-compound. The remaining dioxybenzene is *resorcin*, which must be the *meta*- compound.

The rules governing substitution in the benzene molecule are discussed in the article AROMATIC SERIES. Derivatives of benzene are described, as ANILINE, PHENOL, BROMO-, BROMO-NITRO-, CHLORO-, CHLORO-NITRO-, IODO-, METHYL-, NITRO-, OXY- BENZENE, etc.

BENZENE HEXABROMIDE $C_6H_6Br_6$. Bromine is dropped into boiling benzene exposed to direct sunlight; the hexabromide crystallises out on cooling; it is separated from tri-bromobenzene by sublimation, and finally crystallised from a mixture of alcohol and benzene (Mitscherlich, *P.* 35, 374; Meunier, *C. R.*, 101, 378; *A. Ch.* [6] 10, 269). Prisms, isomorphous with the (α)-hexachloride; not attacked by HNO_3 or H_2SO_4. Alcoholic KOH splits it up into HBr and *u*-tri-bromo-benzene. If the product of the action of $ZnEt_2$ upon benzene hexabromide dissolved in benzene be oxidised with chromic-mixture, benzoic, isophthalic, terephthalic, and di-bromobenzoic acids are formed (Ador a. Rilliet, *Bl.* [2] 24, 485).

BENZENE CARBOXYLIC ACIDS v. BENZOIC, PHTHALIC, *Tri*-MELLITIC, *Tri*-MESIC, *Hemi*-MELLITIC, PREHNITIC, PYROMELLITIC, MELLOPHANIC, and MELLITIC ACIDS.

Benzene penta-carboxylic acid $C_{11}H_6O_{10}$ *i.e.* $C_6H(CO_2H)_5$. Formed by oxidation of pentamethyl benzene (Friedel a. Crafts, *A. Ch.* [6] 1, 474). Amorphous (containing 6aq). The K salt forms small deliquescent prisms; the salts of Ag, Pb, Ba, Fe, Cu, and Al form insoluble pps.

BENZENE (α)-HEXACHLORIDE $C_6H_6Cl_6$. Mol. w. 291. [157°]. S.G. 1·87. Prepared by chlorinating benzene in direct sunlight (Faraday, *A. Ch.* [2] 30, 275; Mitscherlich, *P.* 35, 370; Lesimple, *Bl.* [2] 6, 161): 350 g. may be got from 600 g. benzene (Leeds a. Everhart, *A. C. J.* 2, 205). It may be freed from C_6HCl_5 and $C_6H_2Cl_4$ by treatment with H_2SO_4 or HNO_3 (Meunier, *A. Ch.* [6] 10, 223). Monoclinic crystals; may be sublimed. At 288° it boils, splitting up into HCl and (1, 2, 4)-tri-chloro-

benzene. The same decomposition is effected by heating with alcoholic KOH.

Reactions.—1. *Zinc* reduces it, in alcoholic solution, to benzene (Zinin, *Z.* 1871, 284).—2. Fuming *nitric acid* has no action.—3. *Silver acetate* forms crystalline $C_6H_4Cl_3(OAc)_2C_6H_6Cl_6$.

Benzene (β)-**hexachloride** $C_6H_6Cl_6$. [310°]. V.D. 9·28. Formed at the same time as the (α)-compound; when the mixture is sublimed, the (β)-compound sublimes last. If the mixture (4 pts.) be boiled with KCN (3 pts.) and alcohol, the (β)-compound is left while the (α)-compound is decomposed. Regular octahedra, cubes, tetrahedra, or tetrakis-tetrahedra. Alcoholic potash splits it up into HCl and (1, 2, 4)-tri-chloro-benzene, but more slowly than the (α)-compound (J. Meunier, *C. R.* 98, 436; 100, 358).

BENZENE-HYDRAZIMIDO- *v.* pp. 369, 370.

BENZENE - PHENYL - HYDRAZIMIDO - NAPHTHALENE *v.* *Benzene-*AZO-*phenyl-*(β)-*naphthylamine.*

BENZENE-PYROGALLOL-PHTHALEÏN *v.* *Tri*-OXY-TRI-PHENYL-CARBINOL-CARBOXYLIC ANHYDRIDE.

BENZENE-TRI-QUINONE $C_6O_6$4aq. So-called '*oxy-carboxylic acid*' of Lerch. [c. 95°].

Formation.—1. By the action of HNO_3 upon the hydrochloride of tetra-oxy-di-amido-benzene; the yield is 65 p.c.—2. By the action of HNO_3 upon di-imido-di-oxy-quinone $C_6(NH)_2(OH)_2O_2$.—3. By oxidation of hexa-oxy-benzene $C_6(OH)_6$.

Properties.—Colourless microscopic needles. Nearly insoluble in cold water, alcohol, and ether.

Reactions.—By reducing agents it is converted successively into di-oxy-benzene-di-quinone $C_6(OH)_2O_4$, tetra-oxy-benzene-quinone $C_6(OH)_4O_2$, and finally hexa-oxy-benzene $C_6(OH)_6$. On heating to 100° or on boiling with water it evolves CO_2 and yields croconic acid $C_5H_2O_5$ (Nietzki a. Benckiser, *B.* 18, 504).

BENZENE-RESORCIN PHTHALEÏN *v.* *Di*-OXY-TRIPHENYL-CARBINOL-CARBOXYLIC ANHYDRIDE.

BENZENE - SULPH - AMIDO - ANILIDE *v.* BENZENE-SULPHONIC ACID.

BENZENE - SULPH - AMIDO - TOLUIDE *v.* BENZENE-SULPHONIC ACID.

BENZENE SULPHINIC ACID $C_6H_6SO_2$ *i.e.* $C_6H_5SO_2H$. [84°].

Formation.—1. By adding zinc-dust to a cooled alcoholic solution of the chloride of benzene sulphonic acid; the resulting zinc salt is very slightly soluble in water; it is treated with Na_2CO_3; the filtrate is concentrated and the acid ppd. by HCl (Schiller a. Otto, *B.* 9, 1584).—2. From the phenyl-hydrazide of benzene sulphonic acid $PhSO_2N_2H_2Ph$, called also di-phenyl-sulphazide, by boiling with baryta-water (Limpricht, *B.* 20, 1239).—3. By passing SO_2 into a warm mixture of benzene and Al_2Cl_6 (Friedel a. Crafts, *C. R.* 86, 1368; Adrianowsky, *B.* 12, 853).—4. By the action of $ZnEt_2$ on $C_6H_5SO_2Cl$ (Kalle, *A.* 119, 156).—5. From $C_6H_5SO_2Cl$ and $Pb(SEt)_2$, thus:

$$2PhSO_2Cl + 2Pb(SEt)_2 = (PhSO_2)_2Pb + PbCl_2 + S_2Et_2$$

(Schiller a. Otto, *B.* 9, 1636).—6. From diphenyl disulphide and alcohol potash: $2Ph_2S_2 + 4KOH = PhSO_2K + 3PhSK + 2H_2O$ (S. a. O.).

Properties.—Long radiating prisms. Sl. sol. cold, v. sol. hot, water; v. sol. alcohol and ether; acid to test-paper. Above 100° it decomposes.

Reactions.—1. *Water* at 130° gives benzene sulphonic acid and phenyl benzene-thiosulphonate (Otto, *A.* 145, 317); the same reaction takes place slowly in the cold, especially in presence of HCl (Pauly a. Otto, *B.* 10, 2181).—2. *Ethyl mercaptan* at 100° gives di-ethyl di-sulphide and phenyl-ethyl di-sulphide (Otto a. Rössing, *B.* 19, 3136).—3. *Phosphorus pentachloride* reacts thus: $PhSO_2H + PCl_5 = PCl_3 + HCl + PhSO_2Cl$.—4. *Potash fusion* gives benzene and K_2SO_3.—5. *Sodium chloro-acetate* gives phenyl-sulphonyl-acetic acid, $Ph.SO_2.CH_2.CO_2H$.—6. *Sodium di-chloro-acetate* gives phenyl chloro-methyl sulphone $Ph.SO_2.CH_2Cl$.—7. *Methylene iodide* reacts thus: $CH_2I_2 + Ph.SO_2Na = NaI + Ph.SO_2.CH_2I$.—8. *Sodium* αα-*di-chloro-propionate* acting upon sodium benzene sulphinate gives di-phenyl ethylene di-sulphone, $Ph.SO_2.C_2H_4.SO_2.Ph$.—9. *Phenyl-hydrazine* in presence of conc. HClAq forms phenyl benzene-thiosulphonate and the phenyl hydrazide of benzene sulphonic acid (*q. v.*).—10. When H_2SO_4 is added to a solution of $Ph.SO_2Na$ and NO_2Na a pp. is got which may be crystallised from alcohol. It is perhaps $(PhSO_2)_2NOH$. It is sl. sol. cold water, CS_2 or ligroïn, but v. sol. alcohol and ether. At 100° it evolves nitrous acid gas. Boiling water, alkalis, or acids, decompose it into $PhSO_2H$ and nitrous acid (Königs, *B.* 11, 615).—11. Fuming *nitric acid* forms $C_{18}H_{15}NS_3O$, which may be $(Ph.SO_2)_3NO$. It forms crystals, [98·5°], insol. alkalis, sl. sol. alcohol, m. sol. benzene (Otto a. Gruber, *A.* 141, 370; Königs, *B.* 11, 615, 1590).

Salts.—BaA'_2: clumps.—ZnA'_2: tablets, sl. sol. alcohol and ether, sl. sol. water (Kalle).—$ZnA'_2$2aq: insol. cold water (S. a. O.).—AgA'.

Ethyl ether EtA'.—Formed by means of EtOH and HCl, or, together with CO_2, by heating $Ph.SO_2Na$ with $Cl.CO_2Et$. Non-volatile oil. $KMnO_4$ in acetic acid solution oxidises it to $Ph.SO_3Et$ (Otto a. Rössing, *B.* 18, 2495; 19, 1225).

Benzene di-sulphinic acid $C_6H_4(SO_2H)_2$ [1:3]. From [1:3] $C_6H_4(SO_2Cl)_2$, and zinc-dust (Pauly, *B.* 9, 1595). Oil.—BaA''.

BENZENE-SULPH-NITR-ANILIDE *v.* BENZENE-SULPHONIC ACID.

BENZENE SULPHONE *v.* DI-PHENYL-SULPHONE.

BENZENE SULPHONIC ACID $C_6H_6SO_3$ *i.e.* $C_6H_5.SO_3H$. *Phenyl-sulphurous acid.* *Sulpho-benzolic acid.* [42°].

Formation.—1. From benzene and fuming H_2SO_4 (Mitscherlich, *P.* 31, 283, 634; Stenhouse, *Pr.* 14, 351; Wurtz, *C. R.* 64, 749).—2. By the oxidation of benzene sulphinic acid (Otto a. Ostrop, *A.* 141, 369).—3. By the oxidation of phenyl mercaptan: $PhSH + O_3 = PhSO_3H$ (Vogt, *A.* 119, 151).—4. By boiling *p*-diazo-benzene sulphonic acid with alcohol under pressure (R. Schmitt, *A.* 120, 129).—5. Together with phenyl benzene-thiosulphonate by heating benzene sulphinic acid with water at 130° (Otto, *A.* 145, 317):

$$3Ph.SO_2H = PhSO_3H + Ph.SO_2.SPh + H_2O.$$

Preparation.—Benzene (2 pts.) is shaken with fuming H_2SO_4 (3 pts.) with gentle warm-

ing. The acid is separated from undissolved benzene, diluted, and neutralised with $BaCO_3$ or lead carbonate. In the filtrate the Ba, or Pb, salt is decomposed by H_2SO_4 or H_2S respectively.

Properties.—Small, four-sided, deliquescent plates (containing $1\frac{1}{2}$aq).

Reactions.—1. By fusion with *potash*, *soda*, or a mixture of the two, it is converted into phenol. The percentage of phenol obtained increases with the amount of alkali and with the temperature of the fusion. The percentage of phenol is given in this table; one equivalent of acid being used:

KOH	NaOH	Temperature	Phenol
2	—	253°	23
3	—	210°	7
3	—	267°	79
—	3	209°	1
—	3	280°	26
3	3	211°	2
3	3	277°	39
3	3	360°	64
7	—	252°	96

(P. Degener, *J. pr.* 125, 401).—2. The potassium salt distilled with KCN or K_4FeCy_6 gives benzonitrile (Merz, *Z.* [2] 5, 33). 3. *Dry distillation* gives H_2SO_4, benzene, SO_2, and di-phenyl-sulphone.—4. *Dry distillation of the ammonium salt* gives benzene and small quantities of benzene sulphamide, diphenyl, di-phenyl sulphone, phenyl mercaptan, and (traces of) quinoline (Egli, *B.* 18, 575).—5. The potassium salt distilled with $NaNH_2$ gives aniline (Jackson a. Wing, *Am.* 9, 75).—6. Distillation of the Na salt gives di-phenyl sulphide, di-phenyl di-sulphide, phenyl mercaptan, CO_2, and SO_2 (Stenhouse).—7. A mixture of H_2SO_4 and water boiling at 175° converts it into benzene and H_2SO_4 (Armstrong, *C. J.* 45, 151).—8. Fusion with *potassium formate* gives potassium benzoate.

Salts (Freund, *A.* 120, 76; Kalle, *A.* 119, 161).—BaA'_2aq: pearly plates, sl. sol. alcohol.—$CuA'_2$6aq: large blue tables, sol. alcohol.—AgA'8aq: tables.—$ZnA'_2$6aq: six-sided tables.

Methyl ether MeA'. S.G. $\frac{11}{}$ 1·27. Formed by action of NaOMe upon $Ph.SO_2Cl$ in ether (R. Hübner, *A.* 223, 235). Oil.

Ethyl ether EtA'. S.G. $\frac{11}{}$ 1·22. From NaOEt and $PhSO_2Cl$ in ether. Formed also by oxidising $PhSO_2Et$ (Otto a. Rössing, *B.* 19, 1225). Oil, miscible with alcohol, ether, and benzene. Saponified by boiling water.

Propyl ether PrA'. S.G. $\frac{11}{}$ 1·179 (H.).

Phenyl ether PhA'. [35°]. Formed by acting upon $Ph.SO_2Cl$ dissolved in benzene with sodium-phenol. Formed also by action of zinc-dust on a mixture of phenol and $PhSO_2Cl$. Trimetric crystals, $a:b:c = ·6847:1:·8576$. V. sol. benzene, ether, and alcohol, insol. water. Slowly saponified by boiling aqueous KOH; alcoholic NH_3 even at 200° does not affect it. On nitration it gives the nitro-phenyl ether, and also a tri-nitro- derivative [116°] (Schiaparelli, *G.* 11, 66; R. Otto, *B.* 19, 1832).

p-Nitro-phenyl ether $C_6H_5.SO_3.C_6H_4(NO_2)$. [82°]. Formed by nitrating the preceding; or from *p*-nitro-phenol, $ZnCl_2$, and $PhSO_2Cl$ (Schiaparelli, *G.* 11, 70). Sl. sol. cold alcohol.

Chloride $Ph.SO_2Cl$.—*Benzene sulphochloride.* (247°). S.G. $\frac{11}{}$ 1·378. Formed by the action of PCl_5 on a salt of benzene sulphonic acid (Gerhardt a. Chancel, *C. R.* 35, 690), or by passing chlorine into an aqueous solution of $PhSO_2H$ (Otto a. Ostrop). Oil; v. sol. alcohol and ether. Slowly solidifies at 0° forming large rhombic crystals. May be distilled in vacuo, but is much decomposed on boiling under atmospheric pressure. Hardly attacked by water.

Reactions.—1. *Tin* and HCl form phenyl mercaptan.—2. *Sodium amalgam* or $ZnEt_2$ forms a benzene sulphinate.—3. PCl_5 at 210° gives C_6H_5Cl, phosphorus oxychloride, and SO_2Cl_2 (Kekulé a. Barbaglia, *B.* 5, 876).—4. PbO_2 gives at 180° $PbSO_4$ and C_6H_5Cl (Wallach, *A.* 214, 219).—5. *Phenol* (1 mol.) and zinc-dust gives $Ph.SO_2Ph$; phenol ($\frac{1}{2}$ mol.) and $ZnCl_2$ gives $Ph.SO_2.C_6H_4.O.SO_2.Ph$ (?) [123°] (Schiaparelli, *G.* 11, 66).

Bromide $Ph.SO_2Br$. From $PhSO_2H$ and Br (Otto, *A.* 141, 372). Oil.

Amide $Ph.SO_2NH_2$. *Benzene sulphamide. Benzene sulphonamide.* [156°] (Hybbeneth, *A.* 221, 206). S. ·43 at 16°. Formed by the action of NH_3 on the chloride or bromide (Otto a. Ostrop, *A.* 141, 365), or, in small quantities, by heating the ammonium salt at 200° (Stenhouse, *Pr.* 11, 351). Needles (from water) or plates (from alcohol). V. sl. sol. water, sol. hot NH_3Aq, v. sol. alcohol and ether. Ammoniacal $AgNO_3$ gives a pp. of $Ph.SO_2.NHAg$. With PCl_5 the amide gives $Ph.SO_2.NH.PCl_3$ [131°] (Wichelhaus, *B.* 2, 502). Succinyl chloride gives rise to $PhSO_2N:(C_2O_2)C_2H_4$ [160°], whence conc. NH_3Aq produces $Ph.SO_2.N.CO.C_2H_4.CO.NH_2$ [165°] (Gerhardt a. Chancel, *C. R.* 35, 690; Gerhardt a. Chiozza, *A. Ch.* [3] 47, 129).

Benzoyl derivative $Ph.SO_2NHBz$. [147°]. From benzene sulphonamide and BzCl at 145° (Gerhardt, *A.* 108, 214; Wallach, *A.* 214, 210). Prisms (from alcohol). Salt. $PhSO_2NNaBz$. Silky needles (from alcohol). *Reactions.*—1. PCl_5 gives the imido-chloride $Ph.SO_2.N:CCl.Ph$ [80°]. This forms triclinic plates (from benzoline) $a:b:c = ·862:1:?$, $\alpha = 87° 59'$, $\beta = 94° 31'$, $\gamma = 68° 24'$. When this imido-chloride is heated it splits up into benzonitrile and benzene sulpho-chloride (Wallach a. Gossmann, *A.* 214, 210). Aniline converts the imido-chloride into phenyl-sulphonyl-phenyl-benzamidine $(PhSO_2N):C(NHPh).Ph$.—2. The Pb and Ag derivatives are converted by EtI at 100° into the original amide (Remsen a. Palmer, *Am.* 8, 235).

Di-benzoyl derivative $PhSO_2NBz_2$. [105°].

Methylamide $Ph.SO_2NHMe$. An oil, formed by treating the chloride with aqueous methylamine (Romburgh, *R.* 3, 16).

Methyl-nitro-amide $Ph.SO_2.NMe(NO_2)$. [44°]. From the preceding and HNO_3 (S.G. 1·48).

Ethylamide $Ph.SO_2.NEtH$. [58°]. From the chloride and $NEtH_2$ (Romburgh, *R.* 3, 13).

Ethyl-nitro-amide $Ph.SO_2.NEt(NO_2)$. [44°]. Formed by the action of HNO_3 on the preceding or on the succeeding compound. Needles (from alcohol); volatile with steam.

Di-methylamide $C_6H_5.SO_2NMe_2$. [48°].

Di-ethylamide $Ph.SO_2.NEt_2$. [42°].

Anilide $Ph.SO_2NHPh$. [102°] (Wallach, *A.* 214, 221). S. 4·3 at 16°. From the chloride and aniline (Biffi, *A.* 91, 107; Gericke, *A.* 100, 217; Meyer a. Ascher, *B.* 4, 326).

p-Chloro-anilide $PhSO_2.NH.C_6H_4Cl$. [1??°]. From the preceding and PCl_5, or from $PhSO_2Cl$ and *p*-chloro-aniline (Wallach a. Huth, *B.* 9, 425).

o-Nitro-anilide $Ph.SO_2.NH.C_6H_4(NO_2)$ [1:2]. [104°]. From *o*-nitro-aniline and $PhSO_2Cl$ (Lellman, *A.* 221, 16; *B.* 16, 594). Yellow plates, sol. alcohol, glacial HOAc, and $CHCl_3$.

m-Nitro-anilide $Ph.SO_2.NH.C_6H_4(NO_2)$ [1:3]. [132°]. From *m*-nitro-aniline and $PhSO_2Cl$. Flat yellow needles (L.).

p-Nitro-anilide $Ph.SO_2.NH.C_6H_4(NO_2)$ [1:4]. [139°]. From *p*-nitro-aniline and $Ph.SO_2Cl$. Yellow crystals.

o-Amido-anilide $Ph.SO_2.NH.C_6H_4(NH_2)$ [1:2]. [168°]. From the *o*-nitro-anilide by tin and HCl (L.). Needles (from 50 p.c. alcohol). V. sol. alcohol, sl. sol. ligroïn.—B'HCl.

p-Toluide $Ph.SO_2.NH.C_6H_4Me$ [1:4]. [120°]. From the chloride and *p*-toluidine (Wallach a. Huth, *B.* 9, 427).

m-Nitro-p-toluide $Ph.SO_2.NH.C_6H_3Me(NO_2)$ [1:4:3]. [99°]. From the preceding by nitration; or from $Ph.SO_2Cl$ and nitro-*p*-toluidine (Lellmann, *A.* 221, 18). Cubes (from alcohol). Not attacked by alcoholic KOH.

Di-nitro-p-toluide $Ph.SO_2.NH.C_6H_2Me(NO_2)_2$. [178°]. Formed by nitration of the *p*-toluide. Yellow prisms, sl. sol. cold alcohol (Lellmann, *B.* 16, 595). Not attacked by alcoholic KOH.

m-Amido-p-toluide $Ph.SO_2.NH.C_6H_3Me(NH_2)$ [1:4:3]. [146·5°]. From the nitro-compound by tin and HCl. Colourless needles (from dilute alcohol); sl. sol. water.

di-phenyl-amide $Ph.SO_2NPh_2$. [124°]. From $PhSO_2Cl$ and $NHPh_2$ at 200° (Wallach, *A.* 214, 220). Silk-like needles (from alcohol). Sol. alcohol, ether, or benzene, insol. water. Conc. H_2SO_4 forms a blue solution. Insol. HClAq.

Phenyl-hydrazide $C_{12}H_{12}N_2O_2S$ *i.e.* $Ph.SO_2.N_2H_2Ph$. *Phenyl-benzene-sulphazide. Di-phenyl sulphazide.* [148°-150°]. *Formation.*—1. By the action of SO_2 upon diazo-benzene (Kœnigs, *B.* 10, 1531; Wiesinger, *B.* 10, 1715).—2. From benzene sulphonic chloride and phenyl-hydrazine (Fischer, *A.* 190, 132).—3. From benzene-sulphinic acid (*q. v.*) and phenyl-hydrazine hydrochloride (Escales, *B.* 18, 893).—4. By reduction of $C_6H_5.N_2.SO_2.C_6H_5$ with zinc-dust and acetic acid. *Preparation.*—Aniline is dissolved in alcohol saturated with SO_2; the solution is cooled below 0° and a conc. solution of about double the theoretical quantity of KNO_2 is slowly added; after standing for 24-36 hours it is precipitated by water; the yield is 80 p.c. *Properties.*—White felted needles (from alcohol). With NaOEt it gives a very unstable crystalline sodium compound $C_{12}H_{11}NaN_2SO_2$. *Reaction.*—By boiling with aqueous alkalis (*i.e. baryta-water*) it is decomposed into benzene sulphinic acid, benzene, and N_2; $Ph.N_2H_2.SO_2.Ph = PhH + PhSO_2H + N_2$ (E., *B.* 18, 893; Limpricht, *B.* 20, 1238).

BENZENE-*o*-DISULPHONIC ACID $C_6H_6S_2O_6$ *i.e.* $C_6H_4(SO_3H)_2$ [1:2]. From amido-benzene *m*-sulphonic acid by sulphonation, diazotisation, and boiling with alcohol (Drebes, *B.* 9, 552).

Chloride $C_6H_4(SO_2Cl)_2$ ... sided plates.

Amide $C_6H_4(SO_2NH_2)_2$. [233°].

Benzene-*m*-disulphonic acid $C_6H_4(SO_3H)_2$ [1:3].

Formation.—From amido-benzene *p*-sulphonic acid by sulphonation, diazotisation, and heating with alcohol (Zander, *A.* 198, 8).

Preparation.—When benzene or benzene sulphonic acid is treated with fuming H_2SO_4 both *m* and *p* disulphonic acids are formed. The *m* acid is formed chiefly when the temperature is low or when the mixture is kept at a high temperature for a short time only (Buckton a. Hofmann, *C. J.* 9, 255; Barth a. Senhofer, *B.* 8, 754, 1477; 9, 969; Limpricht, *B.* 9, 550; Körner a. Monselise, *B.* 9, 583). Benzene (1 pt.) is freed from thiophene by shaking with conc. H_2SO_4, and is then dissolved in fuming (70 p.c.) sulphuric acid (4 pts.) at 40°. The solution is heated for 2 hours at 275°; cooled; poured into water, and neutralised with lime; $CaSO_4$ is removed by filtration, and the lime salts of the *m* and *p* acid may be separated by crystallisation, the former separating first (Binschedler a. Busch, *Monit. Scient.* 1878, 1169; *cf.* Egli, *B.* 8, 817; Heinzelmann, *A.* 188, 159).

Properties.—Very deliquescent crystals (containing 2½aq). The alkaline salts are v. sol. water.

Salts.—$Na_2A''4aq$.—$K_2A''aq$. S. 66·6 at 100°.—$BaA''2aq$. S. 44·2 at 100°. Large prisms.—$CuA''6aq$: v. sol. water.—$CaA''1\frac{1}{2}aq$.—$ZnA''4aq$.—$PbA''2aq$. S. (of PbA'') 86·2 at 20°.—Ag_2A''.

Reaction.—1. By *fusion* with *potash* or *soda* it is converted into resorcin. The acid is first converted into *m*-phenol sulphonic acid (at 180°). The amount of resorcin formed by fusing this body (1 mol.) with potash (24 mols.) at 270° for 10 minutes is 2·7 p.c., at 270° for 20 minutes it is 21 p.c., and at 250° for 30 minutes it is 26 p.c. When soda, or a mixture of potash and soda, is used, the yield is rather less (Degener, *J. pr.* 128, 318).—2. By *fusion* with *potassium cyanide* the potassium salt is converted into $C_6H_4(CN)_2$, which, when boiled with potash, gives isophthalic acid (Wislicenus a. Brunner, *B.* 4, 984; Ross-Garrick, *Z.* 5, 549; Barth a. Senhofer, *A.* 174, 238; *B.* 8, 754; V. Meyer a. Michler, *B.* 8, 672).

Chloride $C_6H_4(SO_2Cl)_2$. [63°]. From sodium benzene disulphonate and PCl_5 or $S_2O_5Cl_2$ (Heumann a. Köchlin, *B.* 16, 483). Monosymmetrical crystals, $a:b:c = 1·1991:1:0·8688$, $\beta = 85° 44'$ (Otto, *B.* 19, 2424).

Amide $C_6H_4(SO_2NH_2)_2$. [229°]. Needles.

Benzene-*p*-disulphonic acid $C_6H_4(SO_3H)_2$ [1:4]. Prepared as above. The potassium salt distilled with KCN gives di-cyano-benzene, which, on saponification, gives terephthalic acid (Wislicenus a. Brunner, *B.* 4, 984).

Salts.—$K_2A''aq$: thin plates. S. (of K_2A'') 66·6 at 100°.—$BaA''aq$. S. (of BaA'') 7·19 at 100°.—$CaA''aq$.—$CuA''4aq$.—$PbA''aq$. S. (of PbA'') 24·9 at 26°.—$ZnA''4aq$.

Chloride $C_6H_4(SO_2Cl)_2$. [131°]. Needles.

Amide $C_6H_4(SO_2NH_2)_2$. [288°]. Thin scales (from water).

***s*-Benzene-tri-sulphonic acid** $C_6H_3(SO_3H)_3$ [1:3:5]. Prepared by heating 5 pts. of the potassium salt of the mono- or *m*- di-sulphonic acid with a

pts of ordinary H_2SO_4 in an open dish till H_2SO_4 volatilises; this ready sulphonation is probably due to the presence of $KHSO_4$ or of potassium pyrosulphate. By heating the potassium salt with KCN the nitrile of trimesic acid $C_6H_3(CO_2H)_3$ is obtained. NaOH fusion yields phloroglucin. The Ba salt is sparingly soluble in water.

Salts.—K_3A'''3aq.—$Ba_3A'''_2$.—$Ba_3A'''_2$6aq.—Pb_3A_2'''4aq: slender needles, v. sol. water.—Ag_3A'''3aq (Senhofer, *A.* 174, 243).

Chloride: [184°]. *Amide*: [306°] (Jackson a. Wing, *B.* 19, 898).

Benzoyl-amide $C_6H_3(SO_2NHBz)_3$. [285°].

Anilide $C_6H_3(SO_2NPhH)_3$ [237°] (*J. Am.* 9, 346).

Derivatives of the sulphonic acids of benzene are described as—DIAZOBENZENE SULPHONIC ACID (p. 405), SULPHO-BENZENE-AZOXY-BENZENE SULPHONIC ACID (p. 428), AMIDO-, BROMO-, BROMO-AMIDO-, BROMO-NITRO-, CHLORO-, IODO-, METHYL-, NITRO-, PROPYL-, BENZENE SULPHONIC ACIDS.

BENZENE DI-SULPHOXIDE *v.* PHENYL BENZENE-THIOSULPHONATE.

BENZENE SULPHYDRATE *v.* PHENYL MERCAPTAN.

BENZENE THIOSULPHONIC ACID

$C_6H_5.SO_2.SH.$

Preparation.—1. By the action of KHS on benzene-sulphonic chloride.—2. By heating a solution of a salt of benzene-sulphinic acid with sulphur.

Salts.—KA′: v. sol. hot alcohol and water.—NaA′ 1½aq.

Ethyl ether $C_6H_5.SO_2.SEt$. *Ethyl-phenyl-di-sulphoxide.* From the potassium salt and EtBr. Colourless heavy oil. Insol. water, miscible with alcohol and ether. Slowly volatilises with steam. On reduction with zinc and H_2SO_4 in alcoholic solution it gives phenyl mercaptan and ethyl mercaptan. Boiling KOHAq gives benzene sulphinic acid and di-ethyl di-sulphide (Otto, *B.* 15, 127).

Ethylene ether $A'_2C_2H_4$: [85°]. Formed by heating an alcoholic solution of the Na or K salt (2 mols.) with ethylene bromide (1 mol.). Small thin silky needles. Without taste or smell. V. sol. benzene and hot alcohol, far less in cold alcohol. By warming with alcoholic KOH it gives benzene sulphinic acid, ethane di-sulphinic acid $C_2H_4(SO_2H)_2$, and di-ethylene tetra-sulphide $(C_2H_4)_2S_4$. By warming with alcoholic KHS it gives the potassium salt and ethylene mercaptan $C_2H_4(HS)_2$. If the alcoholic solution is warmed with ethylene mercaptan, benzene sulphinic acid and di-ethylene tetra-sulphide are produced. On reduction it gives primarily benzene sulphinic acid and ethylene mercaptan. By warming with alcoholic H_2S it is converted into phenyl tetra-sulphide, ethylene sulphydrate, &c. (Otto a. Rössing, *B.* 20, 2079, 2090).

Phenyl ether $C_6H_5.SO_2.SC_6H_5$. *Benzene di-sulphoxide. Diphenyl di-sulphoxide.* [45°]. Formed by the decomposition of benzene sulphinic acid (*q. v.*) by boiling water, or even by spontaneous decomposition (Pauly a. Otto, *B.* 9, 1639; 10, 2181; 11, 2070). Monosymmetrical prisms, $a:b:c = 1·446:1:1·4709$ (Otto, *B.* 15, 131).

Reactions.—1. By *saponification with alkalis* it is decomposed into benzene sulphinic acid and di-phenyl-di-sulphide:

$$3C_6H_5.SO_2.SC_6H_5 + 2H_2O = 4C_6H_5.SO_2H + (C_6H_5)_2S_2.$$

This probably takes place in two stages:

$$(a)\ 2C_6H_5.SO_2.SC_6H_5 + 2H_2O = 3C_6H_5.SO_2H + C_6H_5.SH.$$

$$(b)\ C_6H_5.SO_2.SC_6H_5 + C_6H_5.SH = C_6H_5.SO_2H + (C_6H_5)_2S_2.$$

The benzene-thiosulphonic-phenyl-ether reacts in the cold with sodium phenyl mercaptide according to the last equation (*b*) (Otto a. Rössing, *B.* 19, 1235).—2. *Zinc-dust* added to an alcoholic solution gives zinc phenyl mercaptide and zinc benzene sulphinate.—3. H_2S forms benzene sulphinic acid, phenyl mercaptan, phenyl tetra-sulphide, &c.—4. *Zinc phenyl mercaptide* added to an alcoholic solution gives di-phenyl di-sulphide and zinc benzene sulphinate.—5. *Phenyl mercaptan* on heating forms di-phenyl di-sulphide and benzene sulphinic acid.—6. *Ethyl mercaptan* at 115° gives di-ethyl di-sulphide, phenyl-ethyl disulphide, di-phenyl di-sulphide, and other products (Otto a. Rössing, *B.* 19, 3137).

BENZENYL ALCOHOL *v. Ortho*-BENZOIC ACID.

BENZENYL-AMIDINE *v.* BENZAMIDINE.

BENZENYL-TRI-AMIDO-BENZENE

$C_{13}H_{11}N_3$ *i.e.* $Ph.C{<}^{NH}_{N}{>}C_6H_3.NH_2$. [240°].

Amido-phenylene-benzamidine. From benzenyl-nitro-phenylene-diamine, tin, and HCl (Hübner, *A.* 208, 309). Needles, v. sl. sol. water, v. sol. alcohol.—B''2HCl.—B''2HNO_3.—$B''H_2SO_4$2aq.

Benzoyl derivative

$Ph.C{<}^{NH}_{N}{>}C_6H_3NHBz$. [125°-214°]. From di-benzoyl-nitro-phenylene-diamine dissolved in HOAc by boiling with tin and HCl (Ruhemann, *B.* 14, 2653). Plates (containing aq. from dilute alcohol). $B'HCl$: needles.

BENZENYL-(β)-AMIDO-α-NAPHTHOL

$C_{17}H_{11}NO$ *i.e.* $C_{10}H_6{<}^{O}_{N}{>}C.C_6H_5$ [122°]. Prepared by reduction of the benzoyl-derivative of *o*-nitroso-(α)-naphthol (Worms, *B.* 15, 1816). Colourless needles. Sublimable. Sol. alcohol and acetic acid, sl. sol. water.

Benzenyl-(α)-amido-(β)-naphthol

$C_{10}H_6{<}^{N}_{O}{>}C.C_6H_5$. [136°].

Formation.—1. As a by-product in the reduction of (α)-nitro-(β)-naphthyl-benzoate.—2. By heating benzoyl-amido-(β)-naphthol.—(Böttcher, *B.* 16, 1936; *C. C.* 1884, 898).

Properties.—Long colourless needles. Sublimable. V. e. sol. alcohol ether, and benzene, sl. sol. petroleum-ether, insol. water. Dissolves in strong acids. Its solutions have a beautiful blue fluorescence. $B'_2H_2Cl_2PtCl_4$: yellow needles.

BENZENYL-(α)-AMIDO-NAPHTHYL MERCAPTAN $C_{10}H_6{<}^{S}_{N}{>}C.C_6H_5$. [103°]. Formed by heating benzoyl-(α)-naphthylamine (2 pts.) with sulphur (1 pt.) for two hours (yield 10 p.c.) (Hofmann, *B.* 20, 1798). Obtained also by oxidation of the thiobenzoyl derivative of (α)-naphthylamine $C_{10}H_7.N:C(SH).C_6H_5$ with potassium ferricyanide (Jacobsen, *B.* 20, 1895). Glistening colourless needles (from alcohol). V. sol. ether, benzene, and hot alcohol. Very weak base.

Picrate $B'C_6H_2(NO_2)_3OH$: [131°]; small orange needles.

Benzenyl-(β)-amido-naphthyl mercaptan $C_{10}H_6<\overset{N}{\underset{S}{}}>C.C_6H_5$. [107°]. Prepared by heating benzoyl-(β)-naphthylamine with sulphur. Felted needles.—$B'_2H_2Cl_2PtCl_4$ (Hofmann, *B.* 20, 1803).

BENZENYL-AMIDO-PHENANTHROL *v.* PHENANTHRENE.

BENZENYL-o-AMIDO-PHENOL $C_{13}H_9NO$ *i.e.* $Ph.C<\overset{O}{\underset{N}{}}>C_6H_4$. [103°]. (c. 315°). From *o*-amido-phenol and BzCl or phthalic anhydride (Ladenburg, *B.* 9, 1526). Plates (from dilute alcohol). Insol. water, sol. dilute H_2SO_4. Split up by HCl at 130° into benzoic acid and *o*-amido-phenol. Its salts are decomposed by water.—$B'_2H_2PtCl_6$.

BENZENYL-DIAMIDO-DIPHENYL $C_{19}H_{14}N_2$ *i.e.* $C_6H_5.C<\overset{N}{\underset{NH}{}}>C_6H_3.C_6H_5$. [198°]. From benzoyl-nitro-*p*-amido-diphenyl, tin, and glacial HOAc (Hübner, *A.* 209, 347). Plates (from alcohol).—B'HCl.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$.

BENZENYL - AMIDO - PHENYLENE DIAMINE *v.* BENZENYL-TRI-AMIDO-BENZENE.

BENZENYL-AMIDO-PHENYL MERCAPTAN $C_{13}H_9NS$ *i.e.* [1:2] $C_6H_4<\overset{N}{\underset{S}{}}>CPh$. [115°]. (c. 360°).

Formation.—1. By heating amido-phenyl mercaptan with BzCl, with benzoic aldehyde (probably benzyl alcohol is also formed), or with benzonitrile (NH_3 being evolved).—2. By heating phenyl-anilido-acetonitrile with sulphur (H_2S and HCN being evolved).—3. In small quantity by the action of benzoyl chloride on methenyl-amido-phenyl mercaptan.—4. From thiobenzoic anilide and alkaline K_3FeCy_6 (Jacobsen, *B.* 19, 1068).

Preparation.—Benzanilide (2 pts.) is heated with S. (1 pt.) for a few hours to boiling. The yield is 50 to 60 p.c. of the benzanilide used.

Properties.—Needles. Weak base. Sol. alcohol, ether, CS_2 and HClAq. Has a pleasant smell of tea-roses and geraniums. It remains almost unaltered on boiling with aqueous acids or alkalis. On fusion with KOH it is decomposed into benzoic acid and *o*-amido-phenyl mercaptan. Salt.—$B'HAuCl_4$.

References.—Hofmann, *B.* 12, 2359; 13, 7, 1236; Tiemann a. Piebst, *B.* 15, 2033.

BENZENYL - AMIDO - THIO - CRESOL *v.* BENZENYL-AMIDO-TOLYL MERCAPTAN.

BENZENYL - AMIDO - THIO - PHENOL *v.* BENZENYL-AMIDO-PHENYL MERCAPTAN.

BENZENYL - TRI - AMIDO - TOLUENE $C_{14}H_{13}N_3$ *i.e.* $Ph.C<\overset{NH}{\underset{N}{}}>C_6H_2Me.NH_2$. $\left[\begin{smallmatrix}4\\5\end{smallmatrix}:1:3\right]$. [183°]. From benzoyl-di-nitro-toluidine, tin, and HCl (Kelbe, *B.* 8, 877). Needles, insol. water.—B'HCl.—$B'H_2SO_4$ aq

BENZENYL-TRI-AMIDO-TOLUENE $Ph.C<\overset{NH}{\underset{N}{}}>C_6H_2Me.NH_2$ $\left[\begin{smallmatrix}4\\3\end{smallmatrix}:1:6\right]$ (?).

Benzoyl derivative $C_{21}H_{17}N_3O$ aq. [195°–218°]. From di-benzoyl-nitro-*m*-tolylene-diamine, tin, and HCl (Ruhemann, *B.* 14, 2656). Needles (from alcohol).

BENZENYL-AMIDO-TOLYL MERCAPTAN $C_{14}H_{11}NS$ *i.e.* $C_6H_3(CH_3)<\overset{N}{\underset{S}{}}>C—C_6H_5$ [125°]. Prepared by heating amido-tolyl mercaptan $C_6H_3Me(SH)NH_2$ [1:3:4] with benzoyl chloride. Slender needles.—B'HCl: tables, decomposed by water.—$(B'HCl)_2PtCl_4$ aq (Hess, *B.* 14, 493).

BENZENYL-AMIDOXIM *v.* BENZ-AMIDOXIM.

DI-BENZENYL TRI-AMINE $C_{14}H_{13}N_3$ *i.e.* $\{Ph.C(NH)\}_2NH$. [109°]. Formed by boiling benzamidine with Ac_2O. Needles (Pinner a. Klein, *B.* 11, 8).

BENZENYL - AMYL - PHENYLENE - DI-AMINE *v.* BENZENYL-PHENYLENE-DIAMINE.

BENZENYL - BROMO - PHENYLENE - DI-AMINE $C_{13}H_9BrN_2$ *i.e.* $C_6H_5C<\overset{NH}{\underset{N}{}}>C_6H_3Br$ $\left[\begin{smallmatrix}1\\2\end{smallmatrix}:4\right]$. [200°]. From benzoyl-bromo-nitro-aniline by reduction (Hübner, *B.* 8, 564; 10, 1710). Small needles, insol. water. — B'HCl. — $B'HNO_3$.—$B'H_2SO_4$.

BENZENYL-DICINNAMYLENE-DI-AMINE $C_{25}H_{22}N_2$ *i.e.*

$$\begin{array}{l}PhCH:CH.CH—NH\diagdown\\ \qquad\qquad\quad|\qquad\qquad CPh\\ PhCH:CH.CH—N\diagup\!\!\diagup\end{array}$$ [207°].

Phenyl-di-styryl-glyoxaline di-hydride. Formed by heating di-benzoyl-dicinnamylene-diamine with potash in a sealed tube (Japp a. Wynne, *C. J.* 49, 470). Faint yellow crystals. Boiled with HCl it forms a hydrochloride, sol. EtHO, which yields a platinochloride $(C_{25}H_{22}N_2,HCl)_2PtCl_4$.

BENZENYL-ETHOXIM-CHLORIDE $C_6H_5CCl:NOEt$ (125°) at 45 mm.; (230°) at 760 mm. V.D. (to H) = 9·26 (obs.). Colourless oil. V. sol. alcohol and ether, insol. water. It is very stable towards water, acids, and alkalis. Formed by the action of $NaNO_2$ and HCl upon the ethyl ether of benzenyl-amidoxim $C_6H_5C(NH_2):NOEt$. By heating with alcoholic NH_3 the parent substance is reproduced. By heating with sodium ethylate it yields benzenyl-ethoxim-ethyl ether $C_6H_5C(OEt):NOEt$ (Tiemann a. Krüger, *B.* 18, 727; 1057).

BENZENYL - ETHOXIM - ETHYL ETHER $C_6H_5.C(OEt):NOEt$. *a-Ethyl-benz-hydroxamic-ethyl ether.* (128°) at 40 mm.; (238°) at 760 mm. V.D. (to H) = 96·75 (obs.). Colourless oil. Insol. water. Formed by heating benzenyl-ethoxim-chloride $C_6H_5.C(NOEt)Cl$ with sodium ethylate. By HCl it is decomposed into benzoic ether and the ethyl-ether of hydroxylamine $H_2N.OEt$ (Tiemann a. Krüger, *B.* 18, 742).

BENZENYL-ETHYL-AMIDINE $C_9H_{12}N_2$ *i.e.* $PhC(NEt).NH_2$. From benzamidine and EtI (Pinner a. Klein, *B.* 11, 7). Oil.—$(B'HCl)_2PtCl_4$.

DI-BENZENYL-IMIDO-AMIDE *v.* DI-BENZENYL-TRIAMINE.

BENZENYL - ETHYL - PHENYLENE - DI-AMINE *v.* BENZENYL-PHENYLENE-DIAMINE.

BENZENYL-METHOXIM-CHLORIDE $C_6H_5.CCl:NOMe$. (225° uncorr.). V.D. 74·95. Formed by the action of HCl and $NaNO_2$ upon the methyl ether of benzenyl-amidoxim $C_6H_5.C(NH_2):NOMe$ (Krüger, *B.* 17, 1689; 18, 1057). Oily fluid. Very volatile with steam. Sol. alcohol, ether, benzene, and ligroin, insol. water.

BENZENYL - METHYL - PHENYLENE - DI-AMINE *v.* BENZENYL-PHENYLENE-DIAMINE.

BENZENYL - NAPHTHYL - AMIDINE v. NAPHTHYL-BENZAMIDINE.

BENZENYL-NAPHTHYLENE-DIAMINE

$C_{17}H_{12}N_2$ *i.e.* $PhC\langle{}^{N}_{NH}\rangle C_{10}H_6$. [210°]. From benzoyl-nitro-(β)-naphthylamine, tin, and HCl in presence of alcohol (Ebell, *A.* 208, 328). Yellowish crystals, sl. sol. water, v. sol. alcohol.

Salts. — B'HCl. — B'HNO$_3$. — B'$_2$H$_2$SO$_4$. — B'C$_5$H$_{11}$I: small needles; NaOHAq or hot water removes the isoamyl iodide.

BENZENYL-OXAMIDINE is BENZENYL-AMIDOXIM (*q. v.*).

BENZENYL - OXIMIDAMIDE is BENZENYL-AMIDOXIM (*q. v.*).

BENZENYL-PHENYL-AMIDINE v. PHENYL-BENZAMIDINE.

BENZENYL-DI-PHENYL-DI-AMINE v. DI-PHENYL-BENZ-AMIDINE.

BENZENYL-o-PHENYLENE-DI-AMINE

$C_{13}H_{10}N_2$ *i.e.* $C_6H_5.C\langle{}^{NH}_{N}\rangle C_6H_4$. [280°].

Anhydro-benzoyl-di-amido-benzene. From benzoyl-o-nitro-aniline, tin, and HCl (Hubner, *A.* 208, 302; 210, 328). Plates (from glacial HOAc). M. sol. alcohol, sl. sol. benzene and water.

Salts.—B'HCl. — B'$_2$H$_2$PtCl$_6$. — B'HI aq.— B'HNO$_3$. – B'$_2$H$_2$SO$_4$ 1½aq.

Reactions. — 1. *Benzoyl chloride* at 200° has no action. — 2. Heated with *cyanogen iodide* and benzene, pale yellow crystals of $Ph.C\langle{}^{N(CN)}_{N}\rangle C_6H_4$ [106°] are formed (Howe, *Am.* 5, 416). — 3. *Methyl iodide* forms $C_{13}H_9MeN_2MeI$, [141°], whence potash forms $C_{13}H_9MeN_2MeOH$ [152°], insol. hot water, sl. sol. cold alcohol. It forms the following crystalline salts: $C_{13}H_9MeN_2MeCl$ aq.— $(C_{13}H_9MeN_2MeCl)_2PtCl_4$.—$C_{13}H_9MeN_2MeI$, [280°]. $C_{13}H_9MeN_2MeNO_3$. — $C_{13}H_9MeN_2MeSO_4H$ aq.— 4. *Ethyl iodide* forms at 180° $C_{13}H_9EtN_2$, m. sol. water. It forms soluble crystalline salts, B'HCl and B'$_2$H$_2$SO$_4$.—5. *Ethyl iodide* at 210° forms $C_{13}H_9EtN_2EtI$, [155°] whence hot potash liberates the crystalline ammonium base $C_{13}H_9EtN_2EtOH$ [132°], insol. water and alkalis, sl. sol. cold alcohol, v. e sol. benzene and ligroïn. Its salts are crystalline and not decomposed by NH$_3$, Na$_2$CO$_3$, or cold KOH, but hot potash liberates the base. Salts.— $C_{13}H_9EtN_2EtCl$ 2aq. — $(C_{13}H_9EtN_2EtCl)_2PtCl_4$. —$C_{13}H_9EtN_2EtI$. — $C_{13}H_9EtN_2EtSO_4H$ aq.— 6. *Isoamyl iodide* at 170° gives $C_{13}H_9(C_5H_{11})N_2$. Salts. — B'HCl. — B'HI. — B'HNO$_3$.— B'H$_2$SO$_4$ 2aq.—7. *Isoamyl iodide* at 165° for 24 hours gives $C_{13}H_9(C_5H_{11})N_2(C_5H_{11})I$, [112°]. The free ammonium base, $C_{13}H_9(C_5H_{11})N_2C_5H_{11}OH$ [81° and 92°] crystallises from alcohol, and is insol. water. Salts.—B'C$_5$H$_{11}$Cl aq (and 3aq).— B'$_2$(C$_5$H$_{11}$)$_2$PtCl$_6$. – B'C$_5$H$_{11}$NO$_3$.HNO$_3$. [90°].— B'C$_5$H$_{11}$I.—8. Conc. *nitric acid* forms a nitro-compound, $C_{13}H_9(NO_2)N_2$, [196°].—9. H$_2$SO$_4$ forms an unstable sulphonic acid.

BENZENYL - PHENYLENE - DIAMINE - p - CARBOXYLIC ACID $C_6H_4\langle{}^{NH}_{N}\rangle C.C_6H_4.CO_2H$.

Slender needles (containing 1½aq). Almost insol. in cold, v. sol. in hot, water. Prepared by the oxidation of toluenyl-phenylene-diamine $C_6H_4\langle{}^{NH}_{N}\rangle C.C_6H_4.CH_3$ with $K_2Cr_2O_7$ and H_2SO_4.

Salts.—BaA'$_2$ 6aq: small needles, sl. sol. water.—CaA'$_2$ 5aq: slender needles. –KA' 7aq: long needles, v. e. sol. water. — AgA': white gelatinous pp.

Reaction.—The silver salt on distillation gives a ketone '*Anhydro-tolyl-ketamine*' $C_{27}H_{18}N_4O$ or

$C_6H_4\langle{}^{NH}_{N}\rangle C.C_6H_4.CO.C_6H_4C\langle{}^{NH}_{N}\rangle C_6H_4$

[277°] which forms salts B''2HCl and B''H$_2$PtCl$_6$.

Ethyl ether EtA'.—[213°]; colourless needles (Stoddard, *B.* 11, 293; Brückner, *A.* 205, 113; Hübner, *A.* 210, 337).

BENZENYL - PHENYL - THIURAMIDOXIM

$C_6H_5.C(NH.CS.NHC_6H_5):NOH$. [163°]. Formed by the combination of phenyl-thio-carbimide with benz-amidoxim (Krüger, *B.* 18, 1060). Plates. V. e. sol. alcohol, ether, and benzene.

BENZENYL-PHENYL-URAMIDOXIM

$C_6H_5.C(NH.CO.NHC_6H_5):NOH$. [115°]. Formed by the combination of phenyl cyanate with benz-amidoxim (Krüger, *B.* 18, 1059). White plates. V. e. sol. alcohol, ether and benzene, insol. cold water.

BENZENYL-TOLYLENE-DIAMINE

$C_{14}H_{12}N_2$ *i.e.* $C_6H_5.C\langle{}^{NH}_{N}\rangle C_6H_3.CH_3$ [1:3:4]. [240°]. From benzoyl-nitro-p-toluidine, tin, and HCl (Hübner, *A.* 208, 316). Also by heating acetophenone with o-tolylene-diamine (Ladenburg a. Rügheimer, *B.* 12, 951). Crystalline, insol. water, v. sol. hot alcohol; may be distilled.

Salts.—B'HCl: needles; sl. sol. cold water and alcohol.—B'$_2$H$_2$SO$_4$: needles; v. sl. sol. cold water.

Reactions.—1. *Methyl iodide* at 240° gives $C_{14}H_{11}MeN_2MeI$, [106°] whence KOH forms $C_{14}H_{11}MeN_2MeOH$ [144°], insol. water, of which base the following salts are crystalline, viz.:

$C_{14}H_{11}Me_2N_2Cl$ 2aq. – $(C_{14}H_{11}Me_2N_2)_2PtCl_6$.— $C_{14}H_{11}Me_2N_2I$.—$C_{14}H_{11}Me_2N_2SO_4H$. Nitrous acid produces a nitro-compound $C_{14}H_{10}(NO_2)Me_2N_2OH$, [165°] (Hübner, *A.* 210, 371) which forms a platinochloride, $(C_{14}H_{10}(NO_2)Me_2N_2Cl)_2PtCl_4$, and reduces to an amido-compound. – 2. *Ethyl iodide* at 300° gives $C_{14}H_{11}Et_2N_2I$, [129°] whence $C_{14}H_{11}Et_2N_2OH$ [153°] and its salts

$C_{14}H_{11}Et_2N_2ClHCl$. – $(C_{14}H_{11}Et_2N_2)_2PtCl_6$.— $C_{14}H_{11}Et_2N_2I$. – $C_{14}H_{11}Et_2N_2SO_4H$ aq.

BENZENYL - p - TOLYL - TOLYLENE - DI-AMINE $\begin{matrix}C_7H_6\\C_7H_7\end{matrix}\rangle{}^{N}_{N}\rangle C.C_6H_5$. [166°]. Needles or prisms. Formed by reduction of benzoyl-nitro-di-tolyl-amine with tin and HCl.

Salts.—B'HClaq.—B'$_2$H$_2$SO$_4$*: prisms (Lellmann, *B.* 15, 832).

BENZENYL-XYLYLENE-DIAMINE

$C_{15}H_{14}N_2$ *i.e.* $C_6H_5.C\langle{}^{N}_{NH}\rangle C_6H_2Me_2$ [5:1:2 / 4]. [195°]. From benzoyl-nitro-xylidine [185°], tin, and glacial HOAc (Hübner, *A.* 208, 320). Needles, insol. water. Boiling fuming HNO$_3$ forms a compound, crystallising in yellow needles [202°].

Salts.—B'HCl.—B'HNO$_3$.—B'$_2$H$_2$SO$_4$.— B'H$_2$C$_2$O$_4$.

$C_6H_5C\lt^{N}_{NH}\gt C_6H_2Me_2$ [315°]. From benzoyl-nitro-xylidine [178°]. Needles. — B'HCl 3aq (Hübner, *B.* 10, 1711).

BENZ-ERYTHRENE $C_{24}H_{18}$ [307°–308°]. Formed in leading benzene through a red-hot tube (Berthelot, *J.* 1866, 541; 1867, 599, 605; Schultz, *B.* 11, 95). Small leaflets. Almost insoluble in alcohol, difficultly soluble in hot acetic acid and in cold benzene.

BENZ-FURIL $C_{12}H_6O_4$ *i.e.* $Ph.CO.CO.C_4H_3O$. [41°]. From benz-furoïn and Fehling's solution at 50° (Fischer, *A.* 211, 229). Yellow needles. V. sol. alcohol or ether (unlike furil). Volatile.

Tetra-bromide $C_{12}H_8O_3Br_4$. [127°–128°]. Yellow needles.

BENZFURILIC ACID $C_{12}H_{10}O_4$ *i.e.* $C_4H_3O.CPh(OH).CO_2H$. From benz-furil and aqueous KOH at 60°. Prisms (from a mixture of ether with light petroleum). Turns brown at 108°. V. sol. ether, alcohol, or chloroform; sl. sol. light petroleum. Its aqueous solution gradually decomposes. The crystals in conc. H_2SO_4 give a blood-red colour, turning brown. The oily residue got on evaporating an ethereal solution of benzfurilic acid gives with conc. H_2SO_4 a reddish-violet colour, water then gives a blackish-blue pp., which dissolves in conc. H_2SO_4 giving a blue colour (E. Fischer, *A.* 211, 231).

BENZ-FUROÏN $C_{12}H_{10}O_3$ *i.e.* Either $Ph.CH(OH).CO.C_4H_3O$ or $C_4H_3O.CH(OH).CO.Ph$. [137°–139°]. From furfurol (18 g.), benzoic aldehyde (20 g.), alcohol (60 g.), water (80 g.), and KCN (4 g.); by boiling for 20 minutes (E. Fischer, *A.* 211, 228, *B.* 13, 1339). Slender prisms (from alcohol). May be distilled. V. sol. hot alcohol, chloroform, or benzene, sl. sol. water or light petroleum. Alcoholic KOH forms a dark-red solution with bluish-green reflex.

BENZGLYCOCYAMINE $C_8H_9N_3O_2$. Formed by boiling the dicyanide of *m*-amido-benzoic acid (*v.* p. 157) with KOHAq (Griess, *B.* 1, 191; 3, 703; *Z.* 4, 725; 6, 728) or by the action of cyanamide on an alcoholic solution of *m*-amido-benzoic acid containing NH_3 (Griess, *B.* 7, 575). Thin white four-sided plates (containing aq). Sl. sol. hot water, v. sl. sol. ether, insol. NH_3Aq, sol. aqueous mineral acids. Boiling baryta converts it into *m*-amido-benzoic acid, urea, NH_3, and uramido-benzoic acid.

Salts.—B'HCl.—$B'_2H_2PtCl_6$.

BENZGLYCOCYAMIDINE $C_8H_7N_3O$, *i.e.* $HN:C\lt^{NH-C_6H_4}_{NH-CO}\gt$. Formed by the prolonged heating of 'ethoxy-cyanamido-benzoyl' (*v.* p. 155) with alcoholic NH_3 at 100°; or by the action of cyanamide on *o*-amido-benzoic acid (Griess, *B.* 1, 191; 2, 415; *Z.* [2] 5, 574; *B.* 7, 574; 8, 322; 13, 977). Nacreous laminæ, v. sl. sol. water, sl. sol. boiling alcohol. Its **nitrate** forms narrow laminæ, v. sl. sol. alcohol. **Platinochloride**: $B'_2H_2PtCl_6$.

***m*-Carboxy-phenyl-benz-glycocyamidine**

$$\begin{array}{l} \quad\quad\quad HN.C_6H_4.CO \\ \quad\quad\quad\quad |\quad\quad\ \ | \\ CO_2H.C_6H_4.NH.C{=\!=}N \end{array}$$

. Formed from a mixture of 'dicyanamido-benzoyl-'

$$\begin{array}{l} HN.C_6H_4.CO \\ \quad |\quad\quad\quad | \\ NC.C{=\!=}N \end{array}$$

and *m*-amido-benzoic acid by long boiling with water. Very small white needles or plates. Insol. neutral solvents. Tolerably strong acid.

Salts.—$A''Ag_2$: white amorphous pp.—A''_2H_2Ba 10aq (Griess, *B.* 18, 2420).

'Imido-phenyl-benz-glycocyamidine' so-called. $HN:C\lt^{NH.C_6H_4.CO}_{NH.C_6H_4.NH}$ [1:3]. Formed by heating cyancarbimidamidobenzoic acid with *o*-phenylene diamine (Griess, *B.* 18, 2414). Six-sided tables. Nearly insol. water, alcohol, and ether. It has both acid and basic properties.

Salts: A'_2Ba.—A'HHCl: white six-sided plates.

BENZHYDRAMIDE *v.* Benzoic aldehyde.

BENZHYDRAZOÏN *v.* Tri-phenyl-hydrazoïn.

BENZHYDROL *v.* Diphenyl carbinol.

BENZHYDROLENE $C_{13}H_{10}$. [210°]. Got by distilling succinate or benzoate of benzhydrol (Linnemann, *A.* 133, 1), is identical with tetra-phenyl-ethane (Zagumenny, *J. R.* 12, 431).

BENZHYDROXAMIC ACID *v.* Hydroxyl-amine.

BENZHYDRYL ACETATE *v.* *Acetyl*-benz-hydrol.

BENZHYDRYLAMINE *v.* Di-phenyl-carbinylamine.

BENZHYDRYL-BENZOIC ACID *v.* Exo-oxy-benzyl-benzoic acid.

BENZHYDRYL CARBOXYLIC ACID *v.* Exo-oxy-benzyl-benzoic acid.

BENZHYDRYL PHENOL *v.* Di-oxy-di-phenyl-methane.

BENZHYDRYL-*iso*-PHTHALIC ACID *v.* Oxy-benzyl-*iso*-phthalic acid.

BENZHYDRYL-PROPIONIC ACID *v.* γ-oxy-γ-phenyl-butyric acid.

BENZHYDRYL-PROPIO-CARBOXYLIC ACID *v.* Oxy-carboxy-phenyl-propionic acid.

BENZIDINE *and derivatives* *v.* Di-amido-diphenyl *and derivatives.*

BENZIL $C_{14}H_{10}O_2 = C_6H_5.CO.CO.C_6H_5$. *Dibenzoyl.* [95°] (Limpricht a. Schwanert); (346°–348° corr.) (Wittenberg a. V. Meyer).

Formation.—1. By passing chlorine into melted benzoïn:- $C_6H_5.CH(OH).CO.C_6H_5 + Cl_2 = C_6H_5.CO.CO.C_6H_5 + 2HCl$ (Laurent, *A. Ch.* [2] 59, 402).—2. By oxidising benzoïn with nitric acid (Zinin, *A.* 34, 188), and in small quantity by the air-oxidation of benzoïn dissolved in alcoholic potash $C_{14}H_{12}O_2 + O = C_{14}H_{10}O_2 + H_2O$ (Limpricht a. Schwanert, *B.* 4, 335).—3. Together with stilbene by heating stilbene dibromide with water to 150°: $3C_6H_5.CHBr.CHBr.C_6H_5 + 2H_2O = C_6H_5.CO.CO.C_6H_5 + 2C_6H_5.CH:CH.C_6H_5 + 6HBr$ (L. a. S., *A.* 145, 338).—4. Together with tolane by heating tolane-dibromide with water to 200°:

$$2C_6H_5.CBr:CBr.C_6H_5 + 2H_2O = C_{14}H_{10}O_2 + C_6H_5.C:C.C_6H_5 + 4HBr$$

(L. a. S., *B.* 4, 380).—5. From tolane-tetrachloride by heating it with glacial acetic acid or with conc. H_2SO_4 to 165°:

$$C_6H_5.CCl_2.CCl_2.C_6H_5 + 2H_2SO_4 = C_{14}H_{10}O_2 + 2SO_2 + 4HCl$$

(Liebermann a. Homeyer, *B.* 12, 1975).—6. By heating benzoyl chloride with sodium amalgam: $2C_6H_5.COCl + Na_2 = C_{14}H_{10}O_2 + 2NaCl$ (Klinger, *B.* 16, 996).

Preparation.—Benzoïn is heated with twice

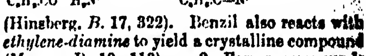
its weight of nitric acid (S.G. 1·4) until it is converted into a clear oily liquid (Zinin). The product is poured into water, and the benzil, which at once solidifies, is purified by recrystallisation from boiling alcohol.

Properties.—Crystallises from hot alcohol in transparent yellow needles; from ether, by spontaneous evaporation, in large six-sided prisms. Insol. water, v. sol. hot alcohol and ether. The crystals are optically active, showing sometimes dextro-rotation, sometimes lævo-rotation, but having no hemihedral faces. Inactive in a fused state or in solution (Descloiseaux, *C. C.* 1870, 418).

Reactions.—1. Benzil is readily attacked by *reducing agents*. *Iron filings and acetic acid*, or *zinc and hydrochloric acid*, acting upon the alcoholic solution, convert it into benzoïn (Zinin, *A.* 119, 177). When heated with alcoholic *potassium hydrosulphide* at 120° it yields a mixture of deoxybenzoïn ($C_6H_5.CH_2.CO.C_6H_5$) and benzoïn (Jena, *A.* 155, 87). *Sodium amalgam* and water convert it into hydrobenzoïn (Zincke a. Forst, *B.* 8, 797). When a solution of benzil in *moist ether* is exposed in a sealed tube to sunlight the benzil is reduced to *benzil-benzoïn* $C_{28}H_{22}O_4$ [134°-135°], which separates in rosettes of white or pale yellow crystals on the sides of the tube, whilst the ether is converted into aldehyde. On melting benzil-benzoïn, or on attempting to recrystallise it from any of the usual solvents, it breaks up into benzil and benzoïn: $C_{42}H_{32}O_6 = 2C_{14}H_{10}O_2 + C_{14}H_{12}O_2$ (Klinger, *B.* 19, 1864). 2. Benzil is very stable towards *acids*. It may be boiled with fuming *hydrochloric acid* without undergoing change; conc. *sulphuric acid* dissolves it, and the addition of water precipitates it unaltered; ordinary strong *nitric acid* does not attack it. On boiling it with fuming nitric acid, however, it yields a mixture of two *dinitrobenzils*, $C_{14}H_8(NO_2)_2O_2$, which may be separated by crystallisation: octahedral crystals [131°], sl. sol. alcohol; and laminæ [147°], less soluble than the foregoing (Zagumenny, *J. R.* 4, 278). An *isodinitrobenzil* [205°] has been indirectly prepared by the oxidation of α- or γ- dinitro-deoxybenzoïn; v. sl. sol. alcohol, m. sol. boiling benzene or glacial acetic acid (Golubeff, *J. R.* 13, 29). A *mononitrobenzil*, $C_{14}H_9(NO_2)O_2$ [110°], has also been indirectly obtained by boiling 1 part of deoxy-benzoïn with 8 parts of nitric acid (S.G. 1·2), or by adding benzoïn to nitric acid (S.G. 1·5) cooled to 0°. Yellow laminæ or flat needles; m. sol. alcohol, more readily in ether. Hot alcoholic potash decomposes it into potassium *m*-azobenzoate and potassium *m*-oxybenzoate:

$$2C_{14}H_9(NO_2)O_2 + 4KHO =$$
$$N_2(C_6H_4.CO_2K)_2 + 2C_6H_5KO_2 + 2H_2O.$$

Tin and hydrochloric acid convert it into *amido-deoxybenzoïn*, $C_{14}H_{11}(NH_2)O$ (Zinin, *A. Suppl.* 3, 153).—3. When heated with *soda-lime*, benzil yields benzene and benzophenone, $CO(C_6H_5)_2$ (Jena, *A.* 155, 87); distilled over heated *litharge* it yields benzophenone (Wittenberg a. V. Meyer, *B.* 16, 501).—4. When benzil is heated with an equal weight of *caustic potash* or *caustic soda* dissolved in 20 parts of water, the benzil slowly dissolves, forming a benzilate (*v.* BENZILIC ACID): $C_6H_5.CO.CO.C_6H_5 + KOH = (C_6H_5)_2C(OH).COOK$. A small quantity of diphenyl-carbinol is formed at the same time by the decomposition of the benzilic acid (Klinger, *B.* 19, ...). *Alcoholic potash* dissolves benzil with a violet colour; on heating, the colour is discharged and the solution contains potassium benzilate. According to Klinger (*loc. cit.*) *aqueous* potash gives this colouration only with benzoïn, and then only when air is admitted. When benzil is dissolved, without heating, in very dilute alcoholic potash (4 grams KOH to the litre) and allowed to stand, with exclusion of air, for about a fortnight, it is converted into a mixture of two compounds, $C_{30}H_{24}O_4$ [200°-201°] (Limpricht a. Schwanert's so-called *ethyl-dibenzoïn*) and $C_{46}H_{34}O_6$ [232°]. The alcohol takes part in the formation of these compounds: $2C_{14}H_{10}O_2 + C_2H_6O = C_{30}H_{24}O_4 + H_2O$, and $3C_{14}H_{10}O_2 + 2C_2H_6O = C_{46}H_{34}O_6 + 4H_2O$. These two substances can be separated by recrystallisation from alcohol, in which the compound $C_{30}H_{24}O_4$ is the more soluble. The compound $C_{30}H_{24}O_4$ is sl. sol. boiling alcohol, sl. sol. boiling benzene, v. sol. boiling glacial acetic acid; deposited from alcohol in colourless granular crystals with 1 mol. of alcohol of crystallisation which is expelled at 120° but not at 100°; crystallises also with 1 mol. of acetic acid and with benzene of crystallisation. The compound $C_{46}H_{34}O_6$ is finally purified by dissolving in boiling phenol and precipitating with alcohol; yellow crystalline powder, v. sl. sol. alcohol, m. sol. boiling phenol (Japp a. Owens, *C. J.* 47, 90; *cf.* also Limpricht a. Schwanert, *B.* 4 335). Benzil also reacts with *isopropyl alcohol*: when it is dissolved in a dilute solution of caustic potash in isopropyl alcohol (2:100) and allowed to stand for some months in a stoppered vessel a compound $C_{31}H_{28}O_4$ [147°-148°] is formed; $2C_{14}H_{10}O_2 + C_3H_8O = C_{31}H_{28}O_4 + O$, a reduction taking place. $C_{31}H_{28}O_4$ forms very lustrous crystals, of rhombohedral habit, v. sl. sol. boiling alcohol (Japp a. Raschen, *C. J.* 49, 832).—5. Benzil reacts with *acetone* in presence of caustic potash, yielding the compounds acetone-benzil, $C_{17}H_{16}O_3$; anhydracetone-benzil, $C_{17}H_{14}O_2$; and anhydracetone-dibenzil, $C_{31}H_{24}O_3$ (*v.* ACETONE-BENZIL, p. 32). With *methyl ethyl ketone* it yields methyl-anhydracetone benzil, $C_{18}H_{16}O_2$: colourless thin prisms [179°]; with *diethyl ketone*, dimethyl-anhydracetone-benzil, $C_{19}H_{18}O_2$: rhomboidal plates [150°]; with *methyl propyl ketone*, ethyl-anhydracetone-benzil, $C_{19}H_{18}O_2$: needles [156°]; with *methyl hexyl ketone*, amyl-anhydracetone-benzil, $C_{22}H_{24}O_2$: silky needles [150·5°]; all sol. alcohol (Japp a. Burton, *C. J.* 51, 431).—6. Benzil reacts with *ammonia*, and also with *aldehydes and ammonia* jointly, to form a number of well-characterised condensation-compounds (*v.* BENZIL, AMMONIA-DERIVATIVES OF). Heated with *aniline* in a sealed tube at 200° it yields *benzil-anilide*, $C_6H_5.C(N.C_6H_5).CO.C_6H_5$ [105°]. Yellow prisms, sol. alcohol (Voigt, *J. pr.* [2] 34, 23).—7. Warmed with (1,2,4)-tolylene-diamine in alcoholic solution it forms *diphenyl-toluquinoxaline*:



(Hinsberg, *B.* 17, 322). Benzil also reacts with *ethylene-diamine* to yield a crystalline compound (Mason, *B.* 19, 113). — 8. Forms compounds

with *hydroxylamine* and with *phenylhydrazine*. Benzil with free hydroxylamine in aqueous-alcoholic solution at the ordinary temperature yields *benzil-mono-oxim* $C_6H_5.C(N.OH).CO.C_6H_5$ [130°–131°], even when an excess of hydroxylamine is employed. Small square white leaflets, v. sol. alcohol and ether, sl. sol. water (Wittenberg a. V. Meyer, *B.* 16, 503). Boiled with hydroxylamine hydrochloride in methyl alcohol, with the addition of one drop of hydrochloric acid, a *dioxim*, *(α)-diphenyl-glyoxim* $C_6H_5.C(N.OH).C(N.OH).C_6H_5$ [237°] separates. Forms lustrous white laminæ, sl. sol. methyl alcohol, alcohol, and ether. Dissolves in conc. caustic soda and is reppd. by acids. Sol. with difficulty in ammonia, the solution giving with silver nitrate a yellow pp. (Goldschmidt a. V. Meyer, *B.* 16, 1617). If benzil, hydroxylamine hydrochloride, and alcohol, acidulated with hydrochloric acid, are heated in a sealed tube for several hours at 170°, an isomeric *(β)-diphenyl-glyoxim* [206°] is formed. White needles, v. sol. boiling alcohol, sl. sol. ether and boiling water. Sol. caustic soda and ammonia. The (α)-compound can be converted into the (β)-compound by heating it with alcohol in a sealed tube at 180°. The nature of this isomerism is not understood; but analogous cases of isomerism have been observed in the benzil and benzoïn groups – thus benzil and isobenzil, hydrobenzoïn and isohydrobenzoïn (Goldschmidt, *B.* 16, 2177). By heating benzil with phenylhydrazine on the water-bath, benzil-di-phenylhydrazide, $C_6H_5.C(N_2H.C_6H_5).C(N_2H.C_6H_5).C_6H_5$ [225°], separates. Faintly yellow needles; v. sol. hot chloroform and benzene, sl. sol. alcohol and ether. Gives a dark-violet colouration with conc. sulphuric acid. Does not regenerate phenylhydrazine when heated with strong hydrochloric acid (Pickel, *A.* 232, 230).—9. When benzil in alcoholic solution is mixed with an excess of nearly anhydrous *hydrocyanic acid* and allowed to stand, large, colourless, tabular, rhombic crystals of *benzil dihydrocyanide*

$$\begin{array}{l}C_6H_5.C(OH).CN\\ \quad|\\ C_6H_5.C(OH).CN\end{array}$$

are deposited (Zinin, *A.* 34, 189). The same compound is formed when an ethereal solution of benzil is mixed with powdered potassium cyanide and conc. hydrochloric acid is added drop by drop, cooling during the operation. Melts at 132°, with decomposition into benzil and hydrocyanic acid. Insol. water and benzene, v. sol. ether and light petroleum. When dissolved in alcohol it is decomposed, even in the cold, into benzil and hydrocyanic acid (Jacoby, *B.* 19, 1519). When finely powdered benzil dihydrocyanide is mixed with a large excess of a concentrated solution of HBr in glacial acetic acid and left for some weeks, a solution is obtained which by spontaneous evaporation deposits lustrous crystals of *di-phenyl-tartramide hydrobromide*

$$\begin{array}{l}C_6H_5.C(OH).CONH_2.HBr\\ \quad|\\ C_6H_5.C(OH).CONH_2\end{array}$$

[185°] and these, when decomposed by ammonia, yield the free *di-phenyl-tartramide*. V. sol. alcohol, v. sl. sol. ether (Burton, *B.* 16, 2232). Pure benzil dihydrocyanide is not hydrolysed by conc. hydrochloric acid, but when an alcoholic solution of benzil, to which an excess of anhydrous hydrocyanic acid has been added, is saturated with gaseous HCl and allowed to stand for some weeks, an acid, $C_{16}H_{13}NO_4$ (colourless prisms, sol. boiling water, melting at 196°), and a compound, $C_{16}H_{12}N_2O$ [196°–197°], are formed. The compound $C_{16}H_{12}N_2O$ forms lustrous pale yellow laminæ or flat needles, sl. sol. boiling water and benzene, v. sol. boiling alcohol. It is feebly basic and forms with hydrochloric acid a colourless salt which is stable only in presence of excess of acid (Japp a. Miller, *C. J.* 51, 29). When benzil is heated with absolute alcohol and hydrocyanic acid at 200° for four hours, it is decomposed into benzoic aldehyde and ethylic benzoate: $C_6H_5.CO.CO.C_6H_5 + C_2H_5.OH = C_6H_5.CHO + C_6H_5.CO_2.C_2H_5$, the hydrocyanic acid apparently undergoing no change. Benzoic acid is also formed (Michael a. Palmer, *Am.* 7, 191). Benzil and alcohol may also be made to react to form benzoic aldehyde and ethylic benzoate by triturating benzil and *potassium cyanide* with alcohol; but in this case a portion of the benzaldehyde is further changed into benzoïn by the action of the potassium cyanide. By neutralising with sodium carbonate the small quantity of benzoic acid which is also formed in this reaction, and which would otherwise decompose the potassium cyanide, 1 part of the cyanide may be made to induce the foregoing change in 50 parts of benzil (Jourdan, *B.* 16, 658).—10. Benzil unites with *nitriles* in presence of conc. sulphuric acid, taking up the elements of water. Thus when powdered benzil (1 mol.) is suspended in conc. sulphuric acid, and propionitrile (2 mols.) is gradually added, cooling during the process, a compound $C_{20}H_{22}N_2O_3$ [197°] is formed: $C_{14}H_{10}O_2 + 2C_3H_5N + H_2O = C_{20}H_{22}N_2O_3$. Lustrous, colourless needles; v. sol. hot alcohol. Boiling with dilute sulphuric acid decomposes it into benzil, propionic acid, and ammonia.—With benzonitrile and sulphuric acid benzil yields a mixture of two compounds which can be readily separated by means of their very different solubilities in hot alcohol: $C_{28}H_{22}N_2O_3$ [168°], analogous to the propionitrile derivative, v. sol. boiling alcohol, crystallises from alcohol in efflorescent oblique prisms of the formula $(C_{28}H_{22}N_2O_3)_2EtOH$; and a compound $C_{28}H_{21}NO_3$ [225°], almost insol. alcohol, v. sol. boiling phenol, sl. sol. boiling benzene, which crystallises from benzene in microscopic, flat rectangular prisms: $2C_{14}H_{10}O_2 + C_7H_5N + H_2O = C_{28}H_{21}NO_3 + C_6H_5.CO_2H$ (Japp a. Tresidder, *B.* 16, 2652).—11. Heated with somewhat more than the equivalent quantity of *phosphorus pentachloride*, benzil yields *dichlorodeoxybenzoïn* *(chlorobenzil)* $C_6H_5.CCl_2.CO.C_6H_5$ [71°]. Short, thick rhombic prisms, insol. water, v. sol. ether, not so readily in alcohol. When heated with alcohol or water to 180° it yields benzil and hydrochloric acid. Zinc and hydrochloric acid, acting on an alcoholic solution, convert the compound into deoxybenzoïn; acetic acid and zinc-dust reduce it first to deoxybenzoïn, and finally to stilbene. PCl_5 at 200° replaces the remaining oxygen atom by Cl_2, yielding tolane tetrachloride, $C_{14}H_{10}Cl_4$ (Zinin, *A.* 119, 177; *J.* 1880, 614; *A.* 149, 374).

Isobenzil.—1. A substance having the same composition as benzil is obtained by acting with sodium amalgam on a solution of benzoyl

chloride in anhydrous ether (Brigel, *A.* 135, 172). Ordinary benzil is formed at the same time (Klinger, *B.* 16, 995). Isobenzil forms colourless tabular monoclinic crystals, also lustrous laminæ or needles [145°–156°], sol. alcohol, ether and CS_2. It is probably a polymeride of benzil, for when treated with bromine it yields benzil (1 mol.) and benzoyl bromide (2 mols.): $C_{28}H_{20}O_4 + Br_2 = C_{14}H_{10}O_2 + 2C_6H_5.COBr$. Heated with alcoholic potash it gives the violet colouration of benzil and is converted into benzilic acid together with a small quantity of benzoic acid (Klinger, *loc. cit.*; also *B.* 19, 1862).—2. By heating benzoic aldehyde with sodium amalgam in an atmosphere of CO_2, Alexéef (*A.* 129, 317) obtained an oil (314° approx.) to which he assigned the formula $C_{14}H_{10}O_2$. S.G. $\frac{12}{}$ = 1·104 (approx.).

F. R. J.

BENZIL, AMMONIA-DERIVATIVES OF. There are four general reactions known, according to which compounds containing the dicarbonyl-group —CO.CO—form condensation-compounds with aldehydes and ammonia jointly. As a knowledge of these reactions is necessary to an understanding not only of the behaviour of benzil with aldehydes and ammonia, but also of that of benzil with ammonia alone, the general equations for these reactions will be introduced at this stage. In the following equations X′ stands for the monad hydrocarbon-radicle of the dicarbonyl-compound, and R′ for the monad hydrocarbon-radicle of the aldehyde:

$$\text{I.}\quad \begin{array}{l} X'.CO \\ \;| \\ X'.CO \end{array} + R'.CHO + NH_3 = \begin{array}{l} X'.C-O \\ \;\;\| \\ X'.C-N \end{array}\!\!\!\!>\!C.R' + 2H_2O.$$

$$\text{II.}\quad \begin{array}{l} X'.CO \\ \;| \\ X'.CO \end{array} + R'.CHO + 2NH_3 = \begin{array}{l} X'.C-NH \\ \;\;\| \\ X'.C-N \end{array}\!\!\!\!>\!C.R' + 3H_2O.$$

$$\text{III.}\quad \begin{array}{l} X'.CO \\ \;| \\ X'.CO \end{array} + 2R'.CHO + 2NH_3 = \begin{array}{l} R'.CH.NH.CO.X' \\ \;\;| \\ R'.CH.NH.CO.X' \end{array} + 2H_2O.$$

Here the dicarbonyl-compound is broken up into two halves, whilst the two aldehyde-groups become directly united. Lastly:

$$\text{IV.}\quad 2\begin{array}{l} X'.CO \\ \;| \\ X'.CO \end{array} + R'.CHO + 2NH_3 = C_3H_2N_2X'_4R'O_2 + 2H_2O.$$

The constitution of the compounds of the last-mentioned type is unknown (Japp a. Streatfeild, *C. J.* 49, 155; Japp a. Hooker, *C. J.* 45, 673; Japp a. Wynne, *C. J.* 49, 464).

It will be shown later on, that in the reactions of benzil with ammonia a part of the benzil is first broken up with formation of benzoic acid and benzoic aldehyde, which latter then takes part, together with benzil and ammonia, in the final reaction. The benzil-ammonia reactions are therefore in reality benzil-aldehyde-ammonia reactions, and will be more readily understood if the reactions of the latter class are described first.

Reactions of Benzil with Aldehydes and Ammonia:—

Equation I. (*vide supra*).—Benzil gives no reactions according to this equation so long as *free* aldehydes are used, but with *nascent* benzoic aldehyde, produced by the decomposition of a portion of the benzil, it reacts according to this equation, yielding *benzilam*, $C_{21}H_{15}NO$ (*vide infra*). In the case of some other dicarbonyl-compounds, however, such as phenanthraquinone (*q.v.*), this reaction occurs with various free aldehydes.

Equation II.—Benzil reacts according to this equation with *formic aldehyde, acetic aldehyde, isovaleric aldehyde, glyoxal, benzoic aldehyde* (free), and *p-oxybenzoic aldehyde*. The compounds formed are derivatives of glyoxaline $\begin{array}{l} CH-NH \\ \;\| \\ CH-N \end{array}\!\!\!\!>\!CH$.

Thus when benzil and *formic aldehyde* are warmed with ammonia in alcoholic solution at about 40° *diphenylglyoxaline* is formed:

$$\begin{array}{l} C_6H_5.CO \\ \quad| \\ C_6H_5.CO \end{array} + H.CHO + 2NH_3 = \begin{array}{l} C_6H_5.C-NH \\ \quad\;\| \\ C_6H_5.C-N \end{array}\!\!\!\!>\!CH + 3H_2O.$$

[The excess of alcohol and ammonia is expelled by heating; the base is extracted with dilute hydrochloric acid, precipitated with ammonia, and crystallised from hot alcohol. It separates from hot alcohol on cooling in long oblique crystals (monosymmetric), and from cold alcohol by evaporation in short lustrous crystals (also monosymmetric, but not referable to the same parameters). [227°]. Monacid base. $(C_{15}H_{12}N_2,HCl)_2,PtCl_4$: pale-yellow, amorphous precipitate, speedily changing into microscopic flat needles (Japp, *C. J.* 51, 558)].—When *acetic aldehyde* is substituted for formic aldehyde in the foregoing reaction, *methyldiphenylglyoxaline*, $\begin{array}{l} C_6H_5.C-NH \\ \quad\;\| \\ C_6H_5.C-N \end{array}\!\!\!\!>\!C.CH_3$, is formed. [Orthorhombic crystals [235°], v. sol. ether and hot alcohol. $(C_{16}H_{14}N_2,HCl)_2,PtCl_4\,2aq$: yellow microscopic needles (Japp a. Wynne)]. The base forms a molecular compound with diphenylglyoxaline (J.)]. Benzil, *isovaleric aldehyde*, and ammonia yield *isobutyldiphenylglyoxaline*, $\begin{array}{l} C_6H_5.C-NH \\ \quad\;\| \\ C_6H_5.C-N \end{array}\!\!\!\!>\!C.CH_2.CH(CH_3)_2$. [Needles [223°], sol. hot benzene and alcohol. $(C_{19}H_{20}N_2,HCl)_2,PtCl_4$: amorphous yellowish-brown precipitate, or small crystals (J. a. W.).] *Glyoxal*, as a dialdehyde, reacts with twice the proportion of benzil and ammonia, forming *tetraphenylglycosine*,

$$\begin{array}{l} C_6H_5.C-NH \\ \quad\;\| \\ C_6H_5.C-N \end{array}\!\!\!\!>\!C.C\!\!<\!\!\begin{array}{l} NH-C.C_6H_5 \\ \qquad\;\| \\ N-C.C_6H_5 \end{array}.$$

[From hot alcohol in tufts of silky needles of the formula $C_{30}H_{22}N_4,C_2H_6O$. Melts above 300°. Feebly basic (Japp a. Cleminshaw, *C. J.* 51, 553)]. Benzil, *benzoic aldehyde*, and ammonia yield

lophine, $\begin{array}{l} C_6H_5.C\text{—}NH \\ \quad\ \ \| \\ C_6H_5.C\text{——}N \end{array}\!\!\!\!>\!C.C_6H_5$ (Radziszewski, *B.* 15, 1493). In a similar manner *p-oxy-benzoic aldehyde* gives *p-oxylophine*,

$$\begin{array}{l} C_6H_5.C\text{—}NH \\ \quad\ \ \| \\ C_6H_5.C\text{——}N \end{array}\!\!\!\!>\!C.C_6H_4(OH).$$

[Tufts of colourless needles [254°–255°], v. sol. hot alcohol, sol. caustic soda, forming a sodium compound. Heated with acetic anhydride, it forms a *mon-acetyl-derivative* $C_{21}H_{15}(C_2H_3O)N_2O$ [229°]; needles, with a faint satiny lustre, sol. hot alcohol. Distilled with zinc-dust, *p*-oxylophine is converted into lophine (Japp a. Robinson, *C. J.* 41, 326)].

Equation III.—Illustrations of this equation are to be found in the reactions of *salicylic aldehyde* and *furfuraldehyde* (pyromucic aldehyde) with benzil and ammonia. *Cinnamic aldehyde* also reacts according to this equation; but in this case another reaction, according to Equation IV., occurs simultaneously.

Thus when equal weights of *salicylic aldehyde* and benzil are dissolved in warm alcohol and the liquid is saturated with gaseous ammonia, the condensation compound *dibenzoyl-dioxystilbene-diamine* separates as a crystalline powder:

$$2C_6H_4(OH).CHO + \begin{array}{l} CO.C_6H_5 \\ | \\ CO.C_6H_5 \end{array} + 2NH_3 =$$
$$\begin{array}{l} C_6H_4(OH).CH.NH.CO.C_6H_5 \\ \qquad\qquad\quad | \\ C_6H_4(OH).CH.NH.CO.C_6H_5 \end{array} + 2H_2O.$$

[It is purified by dissolving it in boiling phenol and precipitating with alcohol. Microscopic plates, melting with decomposition above 300°, insol. in the ordinary organic solvents, sol. boiling phenol, sol. caustic soda, forming a sodium compound. By fusion with *caustic soda* it yields sodium benzoate and sodium salicylate. Heated with dilute *hydrochloric acid* at 210° it is hydrolysed into benzoic acid and *dioxystilbene-diamine* $\begin{array}{l} C_6H_4(OH).CH.NH_2 \\ \qquad\qquad\quad | \\ C_6H_4(OH).CH.NH_2 \end{array}$; small lustrous laminæ [180·5°], v. sol. hot benzene; di-acid base: the Pt salt, $C_{14}H_{16}N_2O_2,2HCl,PtCl_4$4aq forms thick, orange-coloured, rhomboidal plates with bevelled edges, anhydrous at 100°. This base is, however, more readily obtained from its acetyl-derivative (*infra*). When the condensation-compound is boiled with *acetic anhydride* until it dissolves, *dibenzoyl-diacetoxystilbene-diamine* $\begin{array}{l} C_6H_4(O.C_2H_3O).CH.NH(C_7H_5O) \\ \qquad\qquad\qquad\quad | \\ C_6H_4(O.C_2H_3O).CH.NH(C_7H_5O) \end{array}$ is formed (rhomboidal laminæ [225°–227°], sol. acetic acid); and by boiling this compound for eight hours with acetic anhydride the benzoyl-groups are replaced by acetyl-groups yielding *diacetyl-diacetoxystilbene-diamine* $\begin{array}{l} C_6H_4(O.C_2H_3O).CH.NH(C_2H_3O) \\ \qquad\qquad\qquad\quad | \\ C_6H_4(O.C_2H_3O).CH.NH(C_2H_3O) \end{array}$ (prisms [216°–219°] sol. glacial acetic acid and alcohol, deposited from latter solvent with 1 mol. of alcohol of crystallisation). This compound is a tetra-acetyl derivative of the above-mentioned base. By the action of caustic alkali or conc. hydrochloric acid on this tetra-acetyl compound the four acetyl-groups may be removed in successive pairs, yielding first *diacetyl-dioxystilbene-diamine* $\begin{array}{l} C_6H_4(OH).CH.NH(C_2H_3O) \\ \qquad\qquad\quad | \\ C_6H_4(OH).CH.NH(C_2H_3O) \end{array}$ (crystalline powder melting above 300°, sol. hot phenol, sol. caustic alkalis), and finally dioxystilbene diamine. The latter base is most conveniently prepared by heating the tetra-acetyl compound with conc. hydrochloric acid at 120°. By heating the condensation-compound with *benzoic anhydride* a dibenzoyl derivative, corresponding with the diacetyl derivative is obtained; it is a tetra-benzoyl derivative of the base, thus: $\begin{array}{l} C_6H_4(O.C_7H_5O).CH.NH(C_7H_5O) \\ \qquad\qquad\qquad\quad | \\ C_6H_4(O.C_7H_5O).CH.NH(C_7H_5O) \end{array}$. Microscopic plates [246°–248°], sol. acetic acid; sol. dilute caustic potash on long boiling, regenerating the condensation-compound. These various acetyl and benzoyl derivatives may also be synthesised from dioxystilbene-diamine by treatment with acetic anhydride and benzoic anhydride. The dibenzoyl derivative thus prepared is identical with the original condensation-compound (Japp a. Hooker)].

Benzil, *furfuraldehyde*, and ammonia also react according to Equation III.:

$$C_{14}H_{10}O_2 + 2C_5H_4O_2 + 2NH_3 = C_{24}H_{20}N_2O_4 + 2H_2O,$$

forming, however, *two* isomeric compounds of the formula $C_{24}H_{20}N_2O_4$. One of these is an analogue of the salicylic aldehyde compound; it is separated by means of its insolubility in alcohol, and purified by dissolving in boiling phenol and precipitating with alcohol. Crystalline powder, v. sol. hot phenol, sl. sol. glacial acetic acid. The isomeric compound crystallises from alcohol in tufts of silky needles [246°] (J. a. H.).

When *cinnamic aldehyde*, benzil, and ammonia are allowed to react in alcoholic solution, a mixture of two compounds is obtained. Boiling alcohol extracts one of these, and the remaining compound, which is insoluble in alcohol, is purified by dissolving in hot phenol and precipitating with alcohol. The compound soluble in alcohol is *cinnimabenzil*, $C_{23}H_{20}N_2O_2$ (*infra*). The compound insoluble in alcohol is *dibenzoyl-dicinnamylene-diamine* and is formed according to Equation III.:

$$2C_6H_5.CH:CH.CHO + \begin{array}{l} C_6H_5.CO \\ \quad | \\ C_6H_5.CO \end{array} + 2NH_3 =$$
$$\begin{array}{l} C_6H_5.CH:CH.CH.NH.CO.C_6H_5 \\ \qquad\qquad\qquad | \\ C_6H_5.CH:CH.CH.NH.CO.C_6H_5 \end{array} + 2H_2O.$$

Crystalline powder, consisting of short microscopic prisms [264°], insol. in the ordinary organic menstrua, sol. hot phenol. When heated with a solution of *potash* in methyl alcohol at 150°, it parts with the elements of benzoic acid and is converted into *benzenyl-dicinnamylene-diamine*,

$$\begin{array}{l} C_6H_5.CH:CH.CH\text{—}NH \\ \qquad\qquad\qquad\ | \\ C_6H_5.CH:CH.CH\text{——}N \end{array}\!\!\!\!>\!C.C_6H_5.$$

Silky needles, [223°], sol. benzene and alcohol. Monacid base; Pt salt, $(C_{23}H_{22}N_2,HCl)_2,PtCl_4$2aq, forms silky needles.

Equation IV.—The above-mentioned soluble product of the reaction of cinnamic aldehyde

with benzil and ammonia — *cinnimabenzil*, $C_{37}H_{30}N_2O_3$ — is formed according to Equation IV.:

$$2\begin{matrix}C_6H_5.CO\\ |\\ C_6H_5.CO\end{matrix} + C_6H_5.CH{:}CH.CHO + 2NH_3 = C_{37}H_{30}N_2O_3 + 2H_2O.$$

Crystallises from hot alcohol in two forms—slender needles and minute short prisms [188°], sol. benzene. A solution of *potash* in methyl alcohol, when allowed to act upon it in the cold, forms potassium benzoate and *cinnidimabenzil*, $C_{30}H_{26}N_2O_2$:

$$C_{37}H_{30}N_2O_3 + KOH = C_{30}H_{26}N_2O_2 + C_6H_5.COOK.$$

Crystalline powder [283°], sol. hot phenol, precipitated by alcohol. By boiling cinnimabenzil with dilute *sulphuric acid* it is hydrolysed, yielding benzilimide (*infra*), cinnamic aldehyde, benzoic acid, and ammonia: $C_{37}H_{30}N_2O_3 + 2H_2O = \underset{\text{Benzilimide}}{C_{21}H_{17}NO_2} + C_9H_8O + C_7H_6O_2 + NH_3$ (Japp and Wynne).

REACTIONS OF BENZIL WITH AMMONIA ALONE.—Laurent, *Revue Scient* 10, 122; 19, 440; Zinin, *A.* 34, 190; Zincke, *B.* 16, 890; Japp, *B.* 16, 2636; Henius, *A.* 228, 339; Japp a. Wynne, *C. J.* 49, 473.

By heating benzil with alcoholic ammonia the following compounds are obtained: *imabenzil*, $C_{35}H_{28}N_2O_3$; *benzilimide*, $C_{21}H_{17}NO_2$; *benzilam*, $C_{21}H_{15}NO$; and *lophine*, $C_{21}H_{16}N_2$. At the same time benzoic acid, ethylic benzoate, and benzamide are formed. This reaction was first studied by Laurent, who prepared the first three of the above-mentioned compounds, ascribing to them, however, incorrect formulæ.

Benzil is dissolved in alcohol so that the solution is saturated at 40°; gaseous ammonia is passed into the warm liquid to saturation, and the whole is allowed to stand for 24 hours. Prismatic crystals of *imabenzil* are deposited, whilst benzilimide, benzilam, and the other compounds above enumerated remain in solution. If slender acicular crystals of benzilimide should separate they may be removed by warming with alcohol, in which imabenzil is soluble only with difficulty. The formation of imabenzil may be expressed by the equation: $3C_{14}H_{10}O_2 + 2NH_3 = C_{35}H_{28}N_2O_3 + C_6H_5.COOH + H_2O$. *Imabenzil* forms small lustrous orthorhombic prisms [194°], sl. sol. hot alcohol, decomposing on long boiling, and yielding among other products benzilimide; the best solvent is hot methyl alcohol. Boiled with *dilute sulphuric acid* (1 vol. acid : 2 vols. water) it is converted into benzilimide, benzil, and ammonia:

$C_{35}H_{28}N_2O_3 + H_2O = C_{21}H_{17}NO_2 + C_{14}H_{10}O_2 + NH_3$; whilst cold *conc. sulphuric acid* dissolves it, converting it into benzilam, benzaldehyde, benzoic acid, and ammonia:

$$C_{35}H_{28}N_2O_3 + H_2O = C_{21}H_{15}NO + C_7H_6O + C_7H_6O_2 + NH_3$$

(Japp a. Wynne). The formation of benzilam in this reaction was first observed by Laurent. Boiling with alcoholic *potash* converts imabenzil into benzilimide (Laurent). *Acetic acid* and *acetic anhydride* act like dilute sulphuric acid, decomposing it on boiling with formation of benzilimide and benzil (Henius). *Heated* for some time to 140° it decomposes and melts, forming benzilimide, benzilam, and lophine, whilst an odour of benzoic aldehyde is perceptible (H.).

The alcoholic ammoniacal mother-liquor from the preparation of imabenzil yields, when concentrated, a mixture of *benzilimide* and *benzilam*. A similar mixture is obtained by heating benzil with alcoholic ammonia for some hours at 100°, the imabenzil which is first formed being converted into benzilimide and benzilam; at 130° *lophine* is also formed (Henius). The formation of lophine occurs according to the equation $2C_{14}H_{10}O_2 + 2NH_3 =$

$$C_{21}H_{16}N_2 + C_6H_5.COOH + 2H_2O.$$

Benzilimide and benzilam are best separated by boiling the mixture with light petroleum, which extracts the whole of the benzilam, depositing it on cooling, in rosettes of prisms, and hardly dissolves the benzilimide, which may be purified by crystallisation from hot alcohol. *Benzilimide* is formed from benzil and ammonia according to the equation—

$$2C_{14}H_{10}O_2 + NH_3 = C_{21}H_{17}NO_2 + C_6H_5.COOH.$$

Tufts of silky needles [137°–139°] (H.), sol. hot alcohol. Concentrated *sulphuric acid* dissolves it in the cold, abstracting the elements of water, and converting it into benzilam (L.). $C_{21}H_{17}NO_2 - H_2O = C_{21}H_{15}NO$. Heating with *acetic anhydride* produces the same effect (H.). *Chromic mixture* oxidises it to benzoic acid (H.). Benzilimide may also be prepared from imabenzil by Laurent's method of boiling it with alcoholic potash.

Benzilam ($C_{21}H_{15}NO$) may be obtained as above, along with benzilimide, and separated from it as already described, or it may be obtained either from imabenzil or from benzilimide, by the action of cold conc. sulphuric acid. The solution of imabenzil in the cold acid is poured into water, when benzilam separates and may be purified by recrystallisation from alcohol. Most readily obtained by heating benzil with fused ammonium acetate in a flask over a flame until the ammonium salt is volatilised (Japp a. Wilson, *C. J.* 49, 829, footnote); but as some lophine is formed at the same time, the benzilam must be extracted by means of hot light petroleum, in which the lophine is practically insoluble. The formation of benzilam from benzil and ammonia may be expressed thus:

$2C_{14}H_{10}O_2 + NH_3 = C_{21}H_{15}NO + C_6H_5COOH + H_2O$. Well-developed rhombic prisms (from a mixture of ether and alcohol by spontaneous evaporation (H.)); colourless when pure; thin lustrous laminæ, sometimes iridescent, (from hot alcohol); rosettes of prisms (from hot light petroleum). [113°–114°]. Distils at a high temperature without decomposition (L.). V.D. (air = 1) 10·23: calculated 10·28 (J.). With *nitric acid* it yields a mono-nitro- derivative (needles [178°–182°] from benzene) and a dinitro- derivative (H.). *Chromic mixture* oxidises it to benzoic acid (H.).

The above reactions of benzil with ammonia may be explained as follows. In the first place a portion of the benzil is broken up according to the following equations:

$$(a)\ C_6H_5.CO.CO.C_6H_5 + H_2O = \underset{\text{Benzoic acid}}{C_6H_5.COOH} + \underset{\text{Benzoic aldehyde}}{C_6H_5.CHO};$$

$$(b)\ C_6H_5.CO.CO.C_6H_5 + EtOH = \underset{\text{Ethylic benzoate}}{C_6H_5.COOEt} + C_6H_5.CHO;$$

(c) $C_6H_5.CO.CO.C_6H_5 + NH_3 = \underset{\text{Benzamide}}{C_6H_5.CO.NH_2} + C_6H_5.CHO.$

These three compounds—benzoic acid, ethylic benzoate, and benzamide—are always formed in the reaction of benzil with alcoholic ammonia. (The benzamide may also be regarded as having been formed in a secondary reaction, from ethylic benzoate and ammonia.) The benzoic aldehyde, which is the by-product in every case, then reacts, in the nascent state, with benzil and ammonia according to one or other of the following equations:

$$(d)\quad \begin{array}{l} C_6H_5.CO \\ \quad | \\ C_6H_5.CO \end{array} + C_6H_5.CHO + NH_3 =$$

$$\underset{\text{Benzilimide}}{\begin{array}{l} C_6H_5.C-O \\ \quad \| \\ C_6H_5.C-NH \end{array}} \!\!> C(OH).C_6H_5 + H_2O.$$

This reaction of an aldehyde with a dicarbonyl-compound and ammonia, in which *benzilimide* is produced, is not known to occur in the case of free aldehydes.

If the reaction occurs according to Equation I. of the general reactions, *benzilam* is formed:

$$(e)\quad \begin{array}{l} C_6H_5.CO \\ \quad | \\ C_6H_5.CO \end{array} + C_6H_5.CHO + NH_3 =$$

$$\underset{\text{Benzilam}}{\begin{array}{l} C_6H_5.C-O \\ \quad \| \\ C_6H_5.C-N \end{array}} \!\!> C.C_6H_5 + 2H_2O.$$

These formulæ for benzilimide and benzilam account for the readiness with which the former is converted into the latter by the action of dehydrating agents.

If the reaction occurs according to Equation II., *lophine* is produced:

$$(f)\quad \begin{array}{l} C_6H_5.CO \\ \quad | \\ C_6H_5.CO \end{array} + C_6H_5.CHO + 2NH_3 =$$

$$\underset{\text{Lophine}}{\begin{array}{l} C_6H_5.C-NH \\ \quad \| \\ C_6H_5.C-N \end{array}} \!\!> C.C_6H_5 + 3H_2O.$$

Finally, if it occurs according to Equation IV., the product is *imabenzil*:

$$(g)\quad 2\begin{array}{l} C_6H_5.CO \\ \quad | \\ C_6H_5.CO \end{array} + C_6H_5.CHO + 2NH_3 = \underset{\text{Imabenzil.}}{C_{35}H_{26}N_2O_3} + 2H_2O.$$

But *free* benzoic aldehyde, with benzil and ammonia, yields only lophine.

The foregoing equations express the formation of the various compounds obtained from benzil with alcoholic ammonia. The reactions in which the complex compounds discovered by Laurent are formed thus really occur in two stages, of which the first consists in the formation of benzoic aldehyde, the second in a benzil-aldehyde-ammonia condensation (Japp, *B.* 16, 2636; Japp a. Wynne, *C. J.* 49, 477).

F. R. J.

BENZILIC ACID $C_{14}H_{12}O_3 = (C_6H_5)_2C(OH).COOH$. *Diphenylglycollic acid.* [150°] (Jena).

Formation.—1. By warming benzil with alcoholic potash: $C_6H_5.CO.CO.C_6H_5 + KOH = (C_6H_5)_2C(OH).COOK$ (Liebig, *A.* 25, 25; Zinin *A.* 31, 329).—2. By boiling diphenyl-bromo-acetic acid, $(C_6H_5)_2CBr.COOH$ (obtained by passing the vapour of bromine over heated diphenyl-acetic acid), with baryta water (Symons a. Zincke, *A.* 171, 131).

Preparation.—1. Benzil is added to five times its weight of melted potash to which a little water has previously been added. The whole solidifies, owing to the formation of potassium benzilate (E. Fischer, *B.* 14, 326 footnote). The mass is dissolved in water, and the benzilic acid is precipitated by hydrochloric acid and recrystallised from boiling water.—2. It can also be prepared from benzoïn. 15 g. benzoïn, 20 g. KOH and from 250 to 300 c.c. water are heated in a current of air until everything has dissolved. The solution is extracted with ether to remove a small quantity of diphenyl-carbinol which is formed by the decomposition of the benzilic acid, and solid caustic potash is added. This causes the separation of nacreous laminæ of potassium benzilate, which are removed by filtration, washed with a solution of caustic potash, and finally decomposed with sulphuric acid (Klinger, *B.* 19, 1868).

Properties.—Small white monoclinic needles with a satiny lustre. Heated above its melting-point it turns red. Conc. H_2SO_4 colours it deep red; the colour disappears on the addition of water. V. sol. alcohol, ether, and boiling water; sl. sol. cold water. Bitter taste.

Reactions.—1. *Heated* for several hours to 180° it yields a deep-red liquid, and, on cooling, solidifies to an amorphous mass, from which, by treatment with alcohol, *dibenzilic acid* $C_{28}H_{22}O_5$ [196°], benzophenone, and other products can be isolated (Jena).—2. *Chromic mixture* oxidises it to benzophenone:

$$(C_6H_5)_2C(OH).COOH + O = (C_6H_5)_2CO + CO_2 + H_2O.$$

Benzophenone is also produced when silver benzilate is heated, either alone or with water (J.).—3. Heated with *hydriodic acid* (127°) to 150° it is converted into diphenyl-acetic acid:

$$(C_6H_5)_2C(OH).COOH + 2HI = (C_6H_5)_2CH.COOH + I_2 + H_2O.$$

Zinc and hydrochloric acid, and sodium amalgam, are without action (J.).—4. Barium benzilate, distilled with $\frac{1}{10}$th of its weight of *soda-lime*, yields diphenyl-carbinol:

$$(C_6H_5)_2C(OH).COOH = (C_6H_5)_2CH.OH + CO_2$$

(J.).—5. Treated with PCl_5 it yields benzil chloride, $C_{14}H_{11}O_2Cl$, a heavy, colourless liquid (270°), which in contact with moist air is rapidly decomposed into benzilic and hydrochloric acids (Cahours, *A.* 70, 46).

Salts.—Benzilic acid is monobasic. $C_{14}H_{11}O_3K$: v. sol. crystalline salt (Zinin).—$(C_{14}H_{11}O_3)_2Ba6aq$: v. sol. crystalline crusts with a fatty lustre (J.); separates from alcohol in anhydrous needles (Symons a. Zincke).—$(C_{14}H_{11}O_3)_2Pb$: pulverulent precipitate, obtained by adding lead acetate to an aqueous solution of benzilic acid; fuses on heating to a red liquid (Zinin).—$C_{14}H_{11}O_3Ag$: easily decomposable precipitate (J.).

Ethylic benzilate, $C_{14}H_{11}O_3.C_2H_5$. Separates as an oil when a solution of benzilic acid in ethyl alcohol is saturated with gaseous HCl and

then diluted with water. Not volatile without decomposition (J.).

Ethyl-benzilic acid, $C_{16}H_{16}O_3$, isomeric with the foregoing, is a resinous substance obtained by heating benzoïn in alcoholic solution with sodium ethoxide at 150°. Scarcely soluble in potash and ammonia, save in presence of alcohol (Jena a. Limpricht, *A.* 155, 96).

Dibenzilic acid, $C_{28}H_{22}O_5$ [196°], obtained by heating benzilic acid to 180° (*v. supra*), crystallises from alcohol in minute needles. It is an anhydride, and, by heating with water at 180°, is converted into benzilic acid (Jena, *B.* 2, 385). F. R. J.

BENZILIMIDE *v.* BENZIL, AMMONIA-DERIVATIVES OF.

BENZIMIDE *v.* BENZOIC ALDEHYDE.

DI-BENZIMIDE OXIDE *v.* BENZONITRILE.

BENZIMIDO-ACETATE *v.* BENZONITRILE, *Combination* 6.

BENZIMIDO-BENZOATE *v.* BENZONITRILE, *Reaction* 5.

BENZIMIDO-BUTYL-ETHER *v.* BENZONITRILE, *Combination* 5.

BENZIMIDO-ETHYL-ETHER *v.* BENZONITRILE, *Combination* 5.

BENZIMIDO - NAPHTHYLAMIDE *v.* NAPHTHYL-BENZAMIDINE.

BENZO-ANILINE *v.* AMIDO-BENZOPHENONE.

BENZO-TRI-CHLORIDE $C_7H_5Cl_3$ *i.e.* $C_6H_5.CCl_3$. Mol. w. 195·5. (214°). S.G. ^{14} 1·38.

Formation.—1. From benzoyl chloride and PCl_5 (Wöhler a. Liebig, *A.* 3, 265; Schischkoff a. Rosing, *C. R.* 46, 367; Limpricht, *A.* 134, 55; 135, 80; *Bl.* 1866, ii. 468).—2. From benzylidene chloride by chlorination (Cahours, *C. R.* 56, 703).—3. By chlorination of toluene (Naquet, *C. R.* 55, 407; 56, 482).

Preparation.—By passing chlorine (3 mols.) into cold toluene (1 mol.) exposed to direct sunshine (Schramm, *B.* 18, 608) or into boiling toluene.

Properties.—Pungent liquid, insol. water, which slowly converts it into benzoic acid (the change is rapid at 140°). Alcohol at 130° forms benzoic ether.

Reactions.—1. *Sodium* has no action.—2. Ag_2O forms benzoic anhydride.—3. *Aqueous ammonia* at 140° gives benzoic acid, benzamide, and benzonitrile, reacting thus: $C_6H_5CCl_3 + 4NH_3 = 3NH_4Cl + C_6H_5CN$.—4. *Aniline* forms di-phenyl-benzamidine, $C_6H_5C(NC_6H_5).NHC_6H_5$.—5. Reacts with *aromatic bases* thus: $C_6H_5CCl_3 + 2C_6H_5NXY = C_6H_5CCl(C_6H_4NXY)_2 + 2HCl =$

$$C_6H_5.C\begin{cases}C_6H_4.NXY\\C_6H_4.NXYCl\end{cases} + 2HCl;$$ whence KOH

forms the carbinol $C_6H_5C(OH)(C_6H_4NXY)_2$. The reaction requires presence of a metallic chloride or other condensing agent; it takes place most easily with tertiary bases, least readily with primary bases. The products are dyes, the primary bases giving violet, the secondary and tertiary green, colours.—6. It acts similarly on *phenols*: $C_6H_5.CCl_3 + 2C_6H_5OH = 2HCl + C_6H_5CCl(C_6H_4OH)_2$. The products are converted by treatment with water into carbinols $C_6H_5C(OH)(C_6H_4OH)_2$, the alkaline salts of which are colouring matters (Doebner, *A.* 217, 226).—7. Converted by heating with dry *oxalic acid*, first into Ph.CO.Cl, then into $(Ph.CO)_2O$ (Anschütz, *A.* 226, 20).—8. *Copper* produces, on heating, $C_6H_5.CCl_2.CCl_2.C_6H_5$ (Onufrowicz, *B.* 17, 833).

BENZO-CUMIDE *v.* PHENYL AMIDO-CUMYL KETONE.

BENZO-FURILIC ACID *v.* BENZFURILIC ACID.

ISO-BENZOGLYCOL $C_6H_8O_2$ *i.e.* $C_6H_6(OH)_2$(?), [171°]. A crystalline substance formed by the electrolysis of a mixture of benzene, alcohol, and dilute H_2SO_4 (Renard, *C. R.* 91, 175). Sol. water, alcohol, and ether. Reduces Fehling's solution and ammoniacal $AgNO_3$.

Di-acetyl derivative $C_6H_6(OAc)_2$. [121°]. (300°). Insol. water, sol. alcohol and ether.

DI-BENZO-HYDROQUINONE *v.* DI-PHENYL DI-OXY-PHENYLENE DI-KETONE.

BENZOIC ACID $C_7H_6O_2$ *i.e.* $C_6H_5.CO_2H$. Mol. w. 122. [121·4°] (Schiff). (249·2 cor.) (Kopp, *A.* 94, 303). S.G. ^{21} 1·20 (Mendeléeff); 1·337 (Rüdorff, *B.* 12, 250); 1·292 (Schröder, *B.* 12, 562). S. ·156 at 0° (Ost, *J. pr.* [2] 17, 232); ·172 at 0°; ·207 at 10°; ·425 at 31°; 1·78 at 75° (Bourgoin, *J. Ph.* [4] 30, 488). S. (ether) 66 at 15°. S. (alcohol) 47 at 15° (Bourgoin, *Bl.* [2] 29, 245). H.F. 94,533 (Stohmann, *J. pr.* [2] 36, 2). S.V. 126 (Ramsay). S.V.S. 112·09 (S.). R_∞ 54·21 (in a 6 p.c. benzene solution, Kanonnikoff).

Occurrence.—In various resins, *e.g.* gum benzoïn, dragon's blood, storax, and balsams of Peru and Tolu (Blaise de Vigenère, *Traité du feu et du sel*, 1608; Liebig a. Wöhler, *A.* 3, 249). In castoreum (Wöhler, *A.* 67, 360), in the spindle-tree (*Euonymus europæus*). In putrid urine (Liebig, *A.* 50, 168). In cranberries (Loew, *J. pr.* [2] 19, 312). In the higher boiling phenolic portion of coal-tar oils (Schulze, *B.* 18, 615).

Formation.—1. By oxidation of benzoic aldehyde, benzyl alcohol, toluene, cinnamic acid, &c.—2. In small quantity, by passing a current of dry CO_2 through a nearly boiling mixture of aluminium chloride and benzene (Friedel a. Crafts, *C. R.* 86, 1368).—3. In small quantity, by the action of H_2SO_4 and MnO_2 on benzene, especially when formic acid is added (Carius, *A.* 148, 51, 59).—4. By distilling calcic phthalate with lime (Depouilly, *Bl.* [2] 3, 163, 469).—5. By the action of H_2SO_4 and MnO_2 on casein or gelatin (Guckelberger, *A.* 64, 80).—6. By fusing potassium benzene sulphonate with sodium formate (V. Meyer, *B.* 3, 112).—7. From benzonitrile by saponification.—8. By passing CO_2 into sodium in bromo-benzene (Kekulé, *A.* 137, 129).

Preparation.—1. From gum benzoïn by sublimation or by extracting with lime-water or acetic acid (Mohr, *A.* 29, 178; Scheele, *Opusc.* 2, 23; Wöhler, *A.* 49, 245; Loew, *J. pr.* 108, 257; Guichard, *Bl.* [2] 19, 357). Some varieties of gum benzoïn contain cinnamic acid, but this acid is absent from the benzoïn of Siam or the Palembang benzoïn from Sumatra; the latter yields 10 p.c. benzoic acid (Saalfeld, *Ar. Ph.* [3] 16, 280). Benzoic acid that has been sublimed from gum benzoïn leaves a small quantity of oily residue when treated with aqueous Na_2CO_3; this oil consists of guaiacol, methyl benzoate, pyrocatechin, acetyl-guaiacol, benzyl benzoate, benzophenone, and benzoyl-guaiacol (Jacobsen, *Ar. Ph.* [3] 22, 366).—2. From hippuric acid. Urine of horses or

oxen is left for some days to putrefy, when the hippuric acid is split up into glycocoll and benzoic acid; milk of lime is added and the liquid concentrated; excess of lime is ppd. by CO_2, and the filtrate ppd. by Fe_2Cl_6; the ferric benzoate is decomposed by HCl. Benzoic acid prepared in this way crystallises in plates and smells of urine, but by sublimation it may be freed from the smell and then crystallises in needles (Dymond, *Ph.* [3] 14, 463).—3. From **benzotrichloride** by decomposing it with water under pressure, with lime or baryta-water, or with $ZnCl_2$ and glacial HOAc (2 mols.) at 100° (Jacobsen, *B.* 13, 2013).—4. From benzyl chloride by boiling with dilute HNO_3 (Lunge a. Petri, *B.* 10, 1275; *cf.* v. Rad, *D. P. J.* 231, 538).

Properties.—Needles or pearly plates. When pure it does not melt under water, but slight impurities greatly affect its physical properties; the so-called salylic acid was impure benzoic acid (Kolbe a. Lautemann, *A.* 115, 187; Kekulé, *A.* 117, 159; Griess, *A.* 117, 34; Reichenbach a. Beilstein, *A.* 132, 309; Kolbe, *J. pr.* [2] 12, 151). Volatile with steam (1 g. passing over with about 2,000 c.c. water). It dissolves in conc. H_2SO_4, and is reppd. by water. It is not attacked by boiling dilute HNO_3 or CrO_3 (which convert cinnamic acid into benzoic aldehyde); its neutral salts give a buff-coloured pp. with Fe_2Cl_6.

Reactions.—1. Passage of the vapour through a *red-hot tube* gives CO_2 and benzene.—2. *Distillation with lime* produces benzene.—3. Fusion with NaOH produces benzene (75 p.c. of the theoretical amount) and a little diphenyl (Barth a. Senhofer, *B.* 12, 1256).—4. Fusion with KOH produces chiefly *p*-oxy-benzoic acid, but also *o*- and *m*- oxy-benzoic acids, oxy-iso-phthalic acid, diphenyl *o*-, *m*-, and *p*- carboxylic acids, and a brown amorphous substance (Barth a. Schreder, *M.* 3, 799).—5. MnO_2 and H_2SO_4 form CO_2, formic acid, and small quantities of phthalic and terephthalic acids (Carius, *A.* 148, 50; Oudemans, *Z.* [2] 5, 84).—6. *Hydrogen peroxide* and H_2SO_4 produce salicylic acid (Hanriot, *C. R.* 102, 1250).—7. Vapours of benzoic acid passed over heated *zinc-dust* form benzoic aldehyde (Baeyer, *A.* 140, 295).—8. *Sodium amalgam* reduces it to benzyl alcohol, and benzoleïc acid $C_7H_{10}O_2$, and an oil $C_{14}H_{14}O_2$ (Kolbe, *A.* 118, 122; Hermann, *A.* 132, 75).—9. PCl_5 forms benzoyl chloride.—10. Distillation with KSCN or $Pb(SCN)_2$ gives benzonitrile.—11. *Benzene* and P_2O_5 at 190° give benzophenone (Kollarits a. Merz, *B.* 5, 447).—12. *Dimethylaniline* and P_2O_5 give $C_6H_5.CO.C_6H_4.NMe_2$ (O. Fischer, *B.* 10, 958). 13. *Chlorine* produces chloro-benzoic acids.—14. *Bromine* forms bromo-benzoic acids.—15. *Iodine* in presence of HIO_3 forms iodobenzoic acid.—16. Conc. HNO_3 forms *m*-nitro-benzoic acid.—17. Fuming H_2SO_4 forms sulphobenzoic acid.—18. In the *animal organism* it is converted into hippuric acid and excreted in the urine (Wöhler).—19. Cr_2F_6 forms di-fluoro-benzoic acid (Jackson a. Hartshorn, *B.* 18, 1993).

Salts. — Benzoic acid decomposes carbonates, but an alcoholic solution of potassium benzoate is decomposed by CO_2. Calcium benzoate gives on distillation benzophenone, and smaller quantities of benzene, anthraquinone, and tetra-phenyl-methane (Kekulé a. Franchimont, *B.* 5, 909). Calcium benzoate distilled with calcium formate gives benzoic aldehyde. Potassium benzoate distilled alone or with sodium formate gives terephthalic and isophthalic acids (Richter, *B.* 6, 876; Conrad, *B.* 6, 1395). Cupric benzoate gives on distillation benzene, benzoic acid, di-phenyl oxide Ph_2O, phenyl benzoate PhOBz, and phenol (List a. Limpricht, *A.* 90, 190). Cyanogen bromide acts upon potassium benzoate thus: $Ph.CO_2K + CNBr = Ph.CN + CO_2 + KBr$ (Cahours, *A. Ch.* [3] 52, 201). Potassium benzoate when electrolysed gives K and benzoic anhydride; in presence of excess of KOH acetylene is also formed (Bourgoin, *Z.* [2] 4, 566).

$Al_2A'_3(OH)_3aq$: crystals (Sestini, Cicognani, a. Zavatti, *Bl.* [2] 13, 488).—NH_4A': deliquescent; on distillation it gives benzonitrile.—$NH_4HA'_2$.—$BaA'_2 2aq$. — $CdA'_2 2aq$. — $CaA'_2 3aq$: S. 3·5. — $CeA'_2 3aq$. — $CoA'_2 2aq$. — $CuA'_2 2aq$: needles.—$CrA'_2 xaq$.—$CrA'_3 xaq$.—$Cr_2A'_4(OH)_2 2aq$ (Schiff, *A.* 124, 169).—$Fe_2A'_3(OH)_3 6aq$: buff-coloured pp. —$LaA'_3 3aq$. —$PbA'_2 aq$: plates.—$PbA'_2 2PbO$.—$MgA'_2 3aq$: S. 4·5 at 25°.—$MnA'_2 4aq$: large flat prisms, S. 6·55 at 15° (Senbert, *B.* 20, 791). —$HgA'_2 aq$.—$Hg_2A'_2$. — $NiA'_2 3aq$. — $KA' 3aq$.— AgA': S. (alcohol) ·5 at 20°. — $NaA' aq$.— $SnA'_2 aq$.—ZnA'_2.

Methyl ether $C_6H_5CO_2Me$. Mol. w. 136. (199°) (Kopp); (195·5) at 768 mm. (Stohmann, *J. pr.* [2] 36, 4). S.G. $\frac{17}{}$ 1·10 (Kopp); $\frac{20}{4}$ 1·0862 (Brühl). S.V. 149·8 (Ramsay). S.H. ·363 + ·00075*t*. H.F. 84,024 (S.). μ_β 1·5289. R_∞ 61·30 (B.). Formed by distilling wood spirit (1 pt.), benzoic acid (2 pts.), and H_2SO_4 (2 pts.) (Dumas a. Peligot, *A. Ch.* [2] 58, 50; Malaguti, *A. Ch.* [2] 70, 387; Carius, *A.* 110, 210).

Ethyl ether $C_6H_5.CO_2Et$. Mol. w. 150. V.D. 5·53 (calc. 5·2) (Troost, *C. R.* 89, 351). (211·2° cor.) (Linnemann, *A.* 160, 208); (211·4°) (Stohmann, *J. pr.* [2] 36, 4). S.G. $\frac{20}{4}$ 1·0473 (Brühl); $\frac{12}{}$ 1·050 (L.). S.H. ·374 + ·00075*t* (R. Schiff, *A.* 234, 300). H.F. 91,693 (St.). μ_β 1·517 (B.). R_∞ 68·82 (B.). Formed by saturating a solution of benzoic acid (3 pts.) in alcohol (2 pts.) with HCl and distilling the liquid. Converted by Br at 270° into benzoic acid and ethylene bromide (Naumann, *A.* 133, 199). Forms crystalline compounds with titanic chloride: $BzOEtTiCl_4$.—$BzOEt 2TiCl_4$.—$TiCl_4 2BzOEt$ (Demarçay, *C. R.* 70, 1414), and with aluminium chloride: $BzOEtAlCl_3$ (Gustavson, *B.* 13, 157; Scheele, *Opuscula*, 2, 141; Dumas a. Boullay, *A. Ch.* [2] 87, 20; Wöhler a. Liebig, *A.* 3, 274; Deville, *A. Ch.* [3] 3, 188).

Propyl ether $C_6H_5CO_2Pr$. (230°). S.G. $\frac{16}{}$ 1·032 (L.); $\frac{15}{}$ 1·025 (S.). H.F. 98,990 (Stohmann, *J. pr.* [2] 36, 4). S.H. ·383 + ·00075*t* (Schiff, *A.* 234, 300).

Isopropyl ether $C_6H_5CO_2Pr$. (218°). S.G. $\frac{0}{}$ 1·023 (Silva. *Bl.* 12, 225). According to Linnemann (*A.* 161, 51) the ether splits up on distillation into propylene and benzoic acid.

n-Butyl ether $C_6H_5.CO_2C_4H_9$. (247·3 cor.). S.G. $\frac{20}{}$ 1·00.

Isobutyl ether. (234°) at 755 mm. S.G. $\frac{15}{}$ 1·002. H.F. 105,628 (St.).

Isoamyl ether $C_6H_5.CO_2C_5H_{11}$. Mol. w. 192. (261°) (Kopp, *A.* 94, 311); (253°) (Stohmann, *J. pr.* [2] 36, 4). V.D. 6·71 (calc. 6·65,

Troost, *C. R.* 89, 351). S.G. ^{11} 1·004 (K.); ^{12} ·993 (K.). H.C. 1,570,048 (St.).

Formed by heating ethyl benzoate with isoamyl alcohol at 230° for 60 hours (Friedel a. Crafts, *Bl.* [2] 2, 100).

Octyl ether $C_6H_5.CO_2C_8H_{17}$. (306°) (Zincke, *A.* 152, 7).

Decyl ether $C_6H_5.CO_2C_{10}H_{21}$. (over 280°) (Borodin, *J.* 1864, 338).

Cetyl ether $C_6H_5.CO_2C_{16}H_{33}$. [30°] (Becker, *A.* 102, 221).

Allyl ether $C_6H_5.CO_2C_3H_5$. (242°) (Zinin, *A.* 96, 362); (230°) (Berthelot a. de Luca, *A.* 100, 360); (280°) (Cahours a. Hofmann, *A.* 102, 297).

Ethylene ether $(C_6H_5.CO_2)_2C_2H_4$. [67°]. (360°).

Propylene ether $(C_6H_5.CO_2)_2C_3H_6$ [72°]. (300°).

Isoamylene ether $(C_6H_5.CO_2)_2C_5H_{10}$.[133°] (Mayer, *Bl.* [2] 2, 451).

Other ethers of benzoic acid are described as benzoyl derivatives of the hydroxylic compounds from which they may be derived.

References.—*V.* also ALDEHYDO-, AMIDO-, BROMO-, BROMO-AMIDO-, BROMO-NITRO-, BROMO-NITRO-OXY-, BROMO-OXY-, BUTYL-, CHLORO-, CHLORO-IODO-, CHLORO-OXY-, CYANO-, FLUORO-, IODO-, IODO-OXY-, NITRO-, NITRO-BUTYL-, NITRO-OXY-, NITRO-PROPYL-, OXY-, SULPHO-, BENZOIC ACID.

Orthobenzoic acid $C_6H_5.C(OH)_3$. *Benzenyl alcohol.*

Ethyl ether $C_6H_5.C(OEt)_3$. (220°–225°). From benzotrichloride and NaOEt at 100° (Limpricht, *A.* 135, 87).

Tri-acetyl derivative $C_6H_5C(OAc)_3$. From $C_6H_5.CCl_3$ and AgOAc. Readily splits up into Ac_2O and $C_6H_5CO.OAc$.

Sulphinide of benzoic acid *v.* IMIDE OF SULPHOBENZOIC ACID.

BENZOIC ALDEHYDE C_7H_6O *i.e.* $C_6H_5.CO.H$. *Benzaldehyde. Oil of bitter almonds.* Mol. w. 106. (179°). S.G. $\frac{20}{4}$ 1·0455 (Brühl); $\frac{15}{4}$ 1·0504 (Mendeléeff, *J.* 1860, 7). S. ·33 (Flückiger, *J.* 1875, 482). μ_β 1·5621. R_∞ 51·65 (B.). H.F. 23,254 (Stohmann, *J. pr.* [2] 36, 3).

Formation.—1. From almonds (*q. v.*).—2. By oxidation of benzyl alcohol (Cannizzaro, *A.* 88, 130), cinnamic acid (Dumas a. Peligot, *A.* 14, 50), and proteids (Guckelberger, *A.* 64, 60, 72, 86).—2. By boiling benzyl chloride with water and nitrate of lead (Lauth a. Grimaux, *A.* 143, 80), nitrate of copper, or sodium nitrate.—3. By heating benzylidene chloride with water or alkalis (Cahours, *C. R.* 56, 222).—4. By mixing benzylidene chloride with conc. H_2SO_4, diluting, and distilling (Oppenheim, *Z.* [2] 5, 411). 5. By passing vapour of benzoic or phthalic acid over heated zinc-dust (Baeyer, *A.* 140, 295). 6. By reducing benzoic acid with $SnCl_2$ (Dusart, *J.* 1862, 263), or sodium amalgam in slightly acid solution (Kolbe, *A.* 118, 122).—7. By distilling calcium benzoate with calcium formate (Piria, *A.* 100, 104).—8. From benzylidene chloride and silver oxalate (Golowkinsky, *A.* 111, 252) or potassium carbonate (Meunier, *Bl.* [2] 38, 159). 9. From toluene by successive treatment with CrO_2Cl_2 and water (Etard, *C. R.* 90, 534).—10. From benzylidene chloride, acetic acid, and $ZnCl_2$:

$$Ph.CHCl_2 + CH_3.CO_2H = Ph.CHO + CH_3COCl + HCl.$$

Preparation.—1. **Benzyl chloride** (1 pt.) is cohobated at 100° with water (10 pts.) and lead nitrate (1½ pts.), a current of CO_2 being passed through the apparatus. The product is distilled and the light oil fractionated. It is shaken with a saturated solution of $NaHSO_3$, and the resulting crystalline compound is washed with alcohol, crystallised from water, and then decomposed by boiling aqueous Na_2CO_3 (Lauth a. Grimaux, *A.* 143, 80; Bertagnini, *A.* 85, 183).—2. Crude benzylidene chloride is heated at 110°–130° with an equivalent quantity of dry oxalic acid, the product is distilled *in vacuo*: $PhCHCl_2 + H_2C_2O_4 = Ph.CHO + 2HCl + CO_2 + CO$ (Anschütz, *A.* 226, 18).—3. A mixture of benzyl chloride (2 mols.) with benzylidene chloride (1 mol.) obtained by chlorinating toluene till the S.G. is 1·175 is boiled with water and MnO_2 (2 mols.) (Schmidt).—4. By heating benzylidene chloride with aqueous KOH under pressure, or by boiling it with milk of lime. 5. **Bitter almonds** are freed from almond oil by pressure. The press-cake (12 pts.) is made into a paste with boiling water (110 pts.); after 15 minutes the paste is allowed to cool. The emulsin is destroyed by boiling, and therefore a second quantity of the press-cake (1 pt.) is mixed with cold water (6 pts.) and added to the first. After 12 hours' maceration the whole is distilled with steam. The yield is 2 p.c. of the press cake (Pettenkofer, *A.* 122, 77; *cf.* Liebig a. Wöhler, *A.* 22, 1). In this operation amygdalin is split up by the unorganised ferment emulsin, the products being benzoic aldehyde, prussic acid, and glucose:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6.$$

Benzoic aldehyde so prepared contains prussic acid, which appears to be combined in the form of the cyanhydrin $C_6H_5.CH(OH).CN$; for a mixture of benzoic aldehyde and prussic acid yields methylamine on reduction, while crude oil of bitter almonds yields amido phenyl-ethane $C_6H_5.CH_2.CH_2.NH_2$; again, a mixture of benzoic aldehyde and prussic acid, on treatment with chlorine, yields $C_6H_4Cl.CO.Cl$, while oil of bitter almonds yields, by similar treatment, $C_6H_5.CH(OH).CO.N:CH.C_6H_5$ (Fileti, *G.* 9, 446). Prussic acid may be removed by shaking with $FeSO_4$ and lime or potash, or by digesting with HgO and water. The aldehyde is then purified by means of $NaHSO_3$ as described under 1.

Properties.—Colourless oil. It is not poisonous. It oxidises rapidly in the air, but the addition of a little prussic acid hinders the oxidation (Dusart, *Bl.* 8, 459). It does not reduce Fehling's solution.

Reactions.—1. *Oxidised* to benzoic acid by air or other oxidising agents. Conc. HNO_3, however, forms *m*- (and a little *o*-) nitro-benzaldehyde.—2. *Aqueous* or *alcoholic potash* gives benzyl alcohol and potassium benzoate.—3. Led over *red-hot pumice* it is split up into CO and benzene (Barreswil a. Boudault, *A.* 52, 360).—4. PCl_5 forms benzylidene chloride (Cahours, *A.* 70, 39). $COCl_2$ acts similarly (Kempf, *J. pr.* [2] 1, 412).—5. *Chlorine* forms benzoyl chloride and a compound of that body with benzoic aldehyde, $C_6H_5CHCl(OBz)$ (Laurent a. Gerhardt, *J.* 1850, 489). *Bromine* acts similarly, forming $C_6H_5.CHBr(OBz)$ [70°] (Liebig a. Wöhler, *A.* 3, 266; Claisen, *B.* 14, 2475).—6. *Succinyl chlo-*

ride produces succinic acid and benzylidene chloride (Rembold, *A.* 138, 189).—7. *Sodium amalgam* reduces it, in presence of water, to benzyl alcohol, hydrobenzoïn, and isohydrobenzoïn.—8. *Potassium cyanide* produces benzoïn. 9. Aqueous HI (S.G. 2·0) at 280° reduces it to toluene (Berthelot, *J.* 1867, 346).—10. H_2S forms thiobenzaldehyde.—11. Aqueous NH_3 forms hydrobenzamide $(C_6H_5CH)_3N_2$.—12. *Ammonium sulphide* forms thiobenzaldine $C_{21}H_{19}NS_2$.—13. NH_3 and sulphide of carbon form $NH_2.CSS.N(CH.C_6H_5)_2$.—14. With *acetic anhydride* and *sodium acetate*, on heating, it forms sodium cinnamate (*v.* PERKIN'S SYNTHESIS, p. 108). The reaction probably takes place in two stages: $C_6H_5CHO + CH_3.CO_2Na =$

$$C_6H_5.CH(OH).CH_2.CO_2Na =$$

$H_2O + C_6H_5.CH{:}CH.CO_2Na$.—15. With Ac_2O and *sodium succinate* it gives the lactone of $CO_2H.CH_2.CH(CO_2H).CH(OH).C_6H_5$.—16. With *sodium isobutyrate* and *isobutyric anhydride* it forms $C_6H_5.CH(OH).CMe_2.CO_2H$, *v.* OXY-PHENYL-VALERIC ACID (Fittig, *A.* 216, 119).—17. With Ac_2O and *sodic butyrate* at 100° it gives only phenyl-angelic acid, whereas at 180° the chief product is cinnamic acid (Slocum, *A.* 227, 53).—18. The reaction $PhCHO + CH_2XY = H_2O + Ph.CH{:}CXY$ takes place under influence of dry HCl or aqueous or alcoholic KOH on condition that X or Y is of the form CO.Z, *e.g.* benzoic aldehyde acting on acetone, mesityl oxide, acetophenone, pyruvic acid, malonic ether, and aceto-acetic ether. Perkin's reaction is of a similar nature. Occasionally intermediate compounds of the form Ph.CH(OH).CHXY are formed (Claisen, *A.* 218, 121).—19. *Sodium malonate* and Ac_2O react in the cold, giving off CO_2 and forming cinnamic acid, as follows: $Ph.CHO + CH_2(CO_2H)_2 = PhCH{:}C(CO_2H)_2 + H_2O = PhCH{:}CH.CO_2H + CO_2 + H_2O$ (Stuart, *C. J.* 43, 404).—20. *Sodium isosuccinate* and Ac_2O act similarly, forming phenyl-iso-crotonic acid:

$$Ph.CHO + CHMe(CO_2H)_2 = Ph.CH{:}CMe.CO_2H + CO_2 + H_2O.$$

21. *Acetyl chloride* and *zinc-dust* form diacetyl-hydrobenzoïn; while benzoyl chloride and zinc dust form di-benzoyl-hydrobenzoïn (Paal, *B.* 15, 1818; 16, 636; 17, 909).—22. Reacts with *nitro-paraffins* thus: $Ph.CHO + H_2C(NO_2).CH_3 = H_2O + PhCH{:}C(NO_2)CH_3$ (Priebs, *A.* 225, 319).—23. A solution of *aniline* in conc. HCl pps. yellow crystals of a molecular compound. They are only stable in presence of conc. HCl (Elbers, *A.* 227, 357). If $SnCl_4$ be also present a compound $(NPhH_2HCl)_2(C_7H_6O)_3SnCl_4$ is formed (E.).—24. *Aniline* forms benzylidene-aniline, $C_6H_5.CH{:}N.C_6H_5$; *o-toluidine* acts similarly. When heated in presence of HCl or $ZnCl_2$ aniline forms di-amido-tri-phenyl-methane. *Dimethylaniline* in presence of $ZnCl_2$ gives $C_6H_5CH(C_6H_4NMe_2)_2$ (Fischer, *B.* 10, 1623); dimethyl *m-* (but not *o-* or *p-*) toluidine behaves similarly (Fischer, *B.* 13, 807).—25. *Ethylene-diamine* forms $(C_6H_5.CH{:}N)_2C_2H_4$ [54°] (Mason, *B.* 20, 267).—26. (β)-*Naphthylamine* forms benzylidene-(β)-naphthylamine and then phenyl-naphthacridine dihydride $PhCH{<}{C_{10}H_6 \atop C_{10}H_6}{>}NH$ (Claisen, *A.* 237, 261).—27. *Resorcin* in presence of HCl forms a resin $C_{20}H_{20}O_4$ (Baeyer, *B.* 5, 25). *Phenol, pyrocatechin, phloroglucin,* and *orcin* act similarly (Michael a. Ryder, *B.* 19, 1388; *Am.* 9, 130).—28. (β)-*Naphthol* left to stand for several days in the cold with an acetic acid solution of benzaldehyde treated with a few drops of HCl forms di-(β)-naphthyl benzaldehydate (di-naphthyl-ortho-benzoic aldehyde) $C_6H_5CH(OC_{10}H_7)_2$ [205°]. It is a crystalline pp., sl. sol. all ordinary solvents; insol. aqueous alkalis. By warming with acetic acid and a few drops of HCl it is converted into the isomeric di-oxy-di-naphthyl-phenyl-methane $C_6H_5.CH(C_{10}H_6.OH)_2$ which at the same time loses H_2O, giving the compound $C_6H_5.CH{<}{C_{10}H_6 \atop C_{10}H_6}{>}O$ (Claisen, *B.* 19, 3317).—29. *Acetone* in presence of aqueous NaOH produces $C_6H_5.CH{:}CH.CO.CH_3$ and the compound $C_6H_5.CH{:}CH.CO.CH{:}CH.C_6H_5$. In general, compounds containing the group $CH_2.CO$ react with benzoic aldehyde, exchanging the H_2 for CHPh (Claisen, *B.* 14, 349, 2468; *v.* BENZYLIDENE-ACETONE).—30. *Prussic acid* forms mandelonitrile or the cyanhydrin of benzoic aldehyde, $C_6H_5.CH(OH)CN$ (*v.* MANDELIC ACID). This is converted by alcohol and HCl into mandelic imido-ether, $C_6H_5.CH(OH).C(NH).OEt$ (Völckel, *A.* 52, 361; Tiemann, *B.* 14, 1967). Benzoic aldehyde (4 vols.) mixed with nearly anhydrous prussic acid (1 vol.) and shaken with alcoholic KOH forms benzimide $C_{24}H_{18}N_2O_3$ [167°], a flocculent substance, insol. water, alkalis, and acids (Laurent, *A. Ch.* [2] 59, 397; 66, 193; Zinin, *A.* 34, 188; *B.* 2, 552; Gregory, *A.* 54, 372). 31. *Hydrogen iodide* forms a pungent compound $C_{21}H_{18}I_4O$ [28°] insol. water (Geuther a. Cartmell, *A.* 112, 20).—32. SO_3 forms a disulphonic acid $C_6H_4(SO_3H)_2.CHO$ (Engelhardt, *J.* 1864, 350).—33. By treatment with a methyl-alcoholic solution of *sodium methylate* a white solid compound $C_6H_5.C(OMe)(OC_7H_7)(ONa)$ is formed. The same body is formed by the action of sodium methylate on benzyl-benzoate or of sodium benzylate on methyl-benzoate. By treatment with acetic acid it is split up into a mixture of benzyl benzoate, methyl benzoate, benzyl alcohol, and methyl alcohol.—34. If benzaldehyde is heated with a small quantity of *sodium benzylate* for several days at 100°, it is slowly polymerised to benzyl benzoate. Probably the compound $C_6H_5.C(OC_7H_7)_2ONa$ is first formed, and then decomposes into benzyl benzoate and sodium benzylate, which latter again reacts upon a further quantity of benzaldehyde, producing more of the intermediate compound, and so on (Claisen, *B.* 20, 646).—35. By boiling with *ammonium formate* it yields tri-, di-, and mono- benzyl-amine and their formyl derivatives, together with other products (Leuchart, *B.* 19, 2128).—36. *Ammonium sulphocyanide* at 140° forms benzylidene-thio-biuret $C_6H_5CH{<}{NH.CS \atop NH.CS}{>}NH$ [237°] (Brodsky, *M.* 8, 27).—37. *Benzene-azo-benzene* and $ZnCl_2$ forms 'benzylidene-benzidine' $C_{26}H_{22}N_2O_2$(?) [239°] (Barzilowsky, *J. R.* 1885, 366).—38. Acts upon an alcoholic solution of *sodium aceto-acetic ether*, forming $C_{22}H_{22}O_5$ [127°], sol. dilute alkalis (Michael, *J. pr.* [2] 35, 450).—39. *Hydrazine-benzoic acid*, $NH_2.NH.C_6H_4.CO_2H$, forms benzylidene-hydrazine-benzoic acid $C_{14}H_{12}N_2O_2$ [172° uncor.] (Roder, *A.* 236, 171).

Combinations. — 1. With **bisulphites**. $C_6H_5CH(OH).SO_3Na\frac{1}{2}aq$. Small crystals, v. e. sol. water, insol. cold alcohol. Decomposed by boiling water, boiling dilute acids, or cold alkalis or alkaline carbonates (Bertagnini, *A.* 85, 188). — $C_6H_5CH(OH).SO_3K$: laminæ. — $C_6H_5.CH(OH).SO_3NH_4aq$: formed by action of SO_2 on an alcoholic solution of hydrobenzamide (Otto, *A.* 112, 305).—$\{C_6H_5.CH(OH).SO_3\}_2Ba2aq$: from the Na salt and $BaCl_2$.—2. With SO_2 and **aniline**: $(C_6H_5CHO)_2(C_6H_7N)_2SO_2$ (Schiff, *A.* 140, 130).—*p*-**Toluidine** forms, similarly, $(C_7H_6O)_2(C_7H_9N)_2SO_2$.—**Amido-acids** shaken with aqueous solutions of SO_2 and benzoic aldehyde form crystalline compounds, *e.g.* (from **glycocoll**), $C_6H_5.CH(OH).SO_3.NH_3.CH_2.CO_2H$, and $C_6H_5.CH(OH).SO_3.NH_3.C_6H_4.CO_2H$ (from amido-benzoic acid) (Schiff, *A.* 210, 123).—3. With **inorganic salts**. $C_7H_6O\,1\frac{1}{2}CaCl_2(?)$ (Ekmann, *A.* 112, 175).—$C_7H_6OBF_3$ (Landolph, *J.* 1878, 621).

Oxim v. BENZALDOXIM.

Phenyl-hydrazide $C_6H_5.CH:N_2HC_6H_5$. [153°]. Formed by adding a solution of phenyl-hydrazine hydrochloride and sodium acetate to an aqueous solution of benzaldehyde; the white pp. is distinctly visible with a solution of 1 pt. of benzaldehyde in 50,000 pts. of water (Fischer, *B.* 17, 574). Can be crystallised from alcohol. Insol. water. *Acetyl derivative* $C_{13}H_{11}N_2Ac$ [120°], long needles (Schroeder, *B.* 17, 2096). *Benzoyl derivative* $C_6H_5.CH:N.NBzPh$: [122°]. Formed from benzaldehyde and *u*-benzyl-phenyl-hydrazine. Very thin silky needles. V. sol. alcohol (Michaelis a. Schmidt, *B.* 20, 1717).

Methyl-phenyl hydrazide PhMeN.N:CH.Ph. [102°–104·5°].—1. Formed in small quantity from the methyl-phenyl-hydrazide of phenyl-glyoxylic acid (*q.v.*) at 120°. Benzoic aldehyde and methyl-aniline are also formed.—2. From benzoic aldehyde and methyl-phenyl-hydrazine in alcoholic solution. White needles (Wallach, *A.* 227, 352).

Derivatives of *Benzoic ortho-aldehyde* are described as BENZYLIDENE derivatives.

BENZOIC ALDEHYDE, AMMONIA-DERIVATIVES OF. The most important of these are *hydrobenzamide*, *amarine*, and *lophine*.

1. HYDROBENZAMIDE $C_{21}H_{18}N_2$ *i.e.* $(C_6H_5.CH)_3N_2$. *Tribenzylidene-diamine*. [110°].

Formation.—By the action of ammonia upon benzoic aldehyde (Laurent, *A. Ch.* [2] 62, 23; 66, 18), upon benzylidene acetate $C_6H_5.CH(O.C_2H_3O)_2$ (Wicke, *A.* 102, 368), or upon benzylidene-dichloride (Engelhardt, *A.* 110, 78).

Preparation.—Benzoic aldehyde, which must be free from hydrocyanic acid, is left for some days in contact with strong aqueous ammonia. The crystalline mass which separates is washed, first with water and then with ether, and finally recrystallised from alcohol. Heat accelerates the action, but diminishes the yield. Equation: $3C_6H_5.CHO + 2NH_3 = (C_6H_5.CH)_3N_2 + 3H_2O$.

Properties.—Crystallises from hot alcohol in colourless rhombic octahedra, which are generally wedge-shaped. Insol. water: sol. alcohol and ether. Has a sweetish taste and is not poisonous.

Reactions.—1. When *heated* for several hours to 120°–130° it is converted into the isomeric amarine (Bertagnini, *A.* 88, 127). By destructive distillation it yields lophine $C_{21}H_{16}N_2$ (Laurent).—2. Boiling with aqueous *potash* converts it into amarine (Fownes, *T.* 1845, 263), whilst alcoholic potash breaks it up into benzoic aldehyde and ammonia. This last decomposition is also effected by prolonged boiling with alcohol alone. Fusion with potash produces very complex decomposition, yielding among other products lophine.—3. Dilute *acids* hydrolyse it readily on boiling, slowly in the cold, into benzoic aldehyde and ammonia. The ease with which this hydrolysis occurs is best accounted for on the assumption that hydrobenzamide is tribenzylidene-diamine.—4. Dry hydrobenzamide absorbs gaseous *hydrochloric acid*. During the process a non-nitrogenous substance volatilises, and the residue, when treated with water, yields benzoic aldehyde and ammonium chloride. If instead of treating the residue with water it is heated, benzonitrile and benzyl chloride distil over, whilst a complex mixture of basic substances remains (Ekmann, *A.* 112, 151; Kühn, *A.* 122, 308).—5. It unites with 2 mols. of *hydrocyanic acid* to form *hydrobenzamide-dihydrocyanide*, a yellow crystalline mass melting at 55°, which, when treated with hydrochloric acid, is decomposed into benzoic aldehyde and phenylamidoacetonitrile: $C_{21}H_{18}N_2 2HCN + H_2O = C_7H_6O + 2C_6H_5.CH(NH_2).CN$, the latter compound being subsequently hydrolysed to the corresponding acid (Plöchl, *B.* 13, 2119). Under other conditions the benzoic aldehyde and phenylamidoacetonitrile thus formed may unite with elimination of water to form *benzoyl-azotide*, $C_{15}H_{12}N_2$, thus: $C_7H_6O + C_6H_5.CH(NH_2).CN = C_{15}H_{12}N_2 + H_2O$ (Plöchl, *B.* 14, 1142). When an ethereal solution of hydrobenzamide is mixed with 1 mol. of hydrocyanic acid, and gaseous hydrochloric acid is passed into the liquid, a hydrochloride of the monohydrocyanide of hydrobenzamide, $C_{21}H_{18}N_2,HCN,HCl$, separates. On boiling this precipitate with concentrated hydrochloric acid, it is decomposed into benzoic aldehyde, ammonia, and the hydrochloride of an anhydride of the formula $C_{15}H_{14}N_2O$:

$$C_{21}H_{18}N_2.HCN + 2H_2O = C_{15}H_{14}N_2O + C_6H_5.CHO + NH_3.$$

The free anhydride melts at 161° and sublimes without decomposition; the acid $C_{15}H_{16}N_2O_2$ melts at 120° (Plöchl, *B.* 14, 1139).—6. Dissolved in absolute alcohol and treated in the cold with 3 p.c. *sodium amalgam* it yields *benzylidene-dibenzylimide* $C_6H_5.CH(NH.CH_2.C_6H_5)_2$. A stronger amalgam, aided by heat, converts it into benzylamine and toluene (O. Fischer, *B.* 19, 748). 7. Hydrobenzamide is also acted upon by *chlorine*, *sulphurous anhydride*, *sulphuretted hydrogen*, and *ethyl iodide*, but the reactions are not of importance.

2. AMARINE: $C_{21}H_{18}N_2$. Isomeric with hydrobenzamide. Probable constitution:

$$\left.\begin{array}{l} C_6H_5.C.NH \\ \quad\;\, \| \\ C_6H_5.C.NH \end{array}\right> CH.C_6H_5$$ (E. Fischer, *A.* 211, 217; Japp a. Robinson, *C. J.* 41, 323); or

$$\left.\begin{array}{l} C_6H_5.CH.NH \\ \quad\;\;\, | \\ C_6H_5.CH{-}N \end{array}\right> C.C_6H_5$$ (Claus, *B.* 15, 2338).

[100°].

Formation.—1. By the action of ammonia upon an alcoholic solution of benzoic aldehyde

(Laurent, *C. R.* 19, 858).—2. By boiling hydrobenzamide with aqueous potash (Fownes, *T.* 1845, 268).—3. By heating hydrobenzamide to 120°-130° (Bertagnini, *A.* 88, 127).—4. Together with lophine by distilling the double compound of benzoic aldehyde and ammonium hydrogen sulphite with excess of slaked lime (Gössmann, *A.* 93, 329).—5. In small quantity when ammonia acts upon a mixture of benzoïn and benzoic aldehyde:—$C_{14}H_{12}O_2 + C_7H_6O + 2NH_3 = C_{21}H_{18}N_2 + 3H_2O$ (Radziszewski, *B.* 15, 1495).

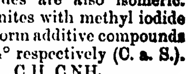
Preparation.—Hydrobenzamide is heated from 2 to 4 hours at 120°-130°. The vitreous mass thus obtained is dissolved in boiling alcohol, and an excess of hydrochloric acid is added. The amarine hydrochloride, which separates in white crystals, is purified by recrystallising from boiling alcohol and is then decomposed with ammonia.

Properties.—Deposited from alcohol in lustrous prisms. Melts at 100° (Fownes), but by boiling for some time with water, is converted into a granular substance melting as high as 126°. This modification is reconverted into prismatic amarine, melting at 100°, by recrystallisation from alcohol (Claus, *B.* 18, 1678). Insol. water, v. sol. alcohol and ether; the alcoholic solution having an alkaline reaction. Has a bitter taste, which is noticeable only after a time. Very poisonous. Combines with acids to form sparingly soluble salts which have an intensely bitter taste. — $C_{21}H_{18}N_2,HCl$. Needles, sparingly soluble in boiling water. — $(C_{21}H_{18}N_2,HCl)_2,PtCl_4$. Yellow crystalline salt (Gössmann). — $C_{21}H_{18}N_2,HI$ (Borodine, *A.* 110, 79). — $C_{21}H_{18}N_2,HNO_3$ (Fownes). $(C_{21}H_{18}N_2)_2H_2SO_4 + 8\frac{1}{2}H_2O$ (Groth, *A.* 152, 122).— $(C_{21}H_{18}N_2)_2,H_2Cr_2O_7$. Yellow precipitate, almost insol. water.

Reactions.—1. By *destructive distillation* it yields ammonia, toluene, and lophine, $C_{21}H_{16}N_2$ (Fownes; *v.* also Radziszewski, *B.* 10, 70).—2. By limited *oxidation*, as when the chromate is boiled with glacial acetic acid, it is converted into lophine: $C_{21}H_{18}N_2 + O = C_{21}H_{16}N_2 + H_2O$ (Fischer a. Troschke, *B.* 13, 707). Excess of chromic acid oxidises it to benzoic acid.—3. When a hot alcoholic solution of amarine is acidified with acetic acid and a hot concentrated solution of an *alkaline nitrite* is added, *nitroso-amarine*, $C_{21}H_{17}(NO)N_2$, separates, and, by recrystallisation from alcohol, may be obtained in rhombic tables, which, when heated to 150°, decompose with formation of lophine (Borodine, *B.* 8, 934).—4. With *nitric acid* in the cold, *mononitro-amarine*, $C_{21}H_{17}(NO_2)N_2$, is formed; hot nitric acid converts it into *dinitro-amarine*, $C_{21}H_{16}(NO_2)_2N_2$. The latter compound yields, with reducing agents, *diamido-amarine*, $C_{21}H_{16}(NH_2)_2N_2$. Salts of these nitro- and amido- bases have been prepared (Claus a. Witt, *B.* 18, 1670).—5. With *acetyl chloride* an ethereal solution of amarine yields a product which, when treated with alcohol, is separated into amarine hydrochloride and diacetyl amarine, $C_{21}H_{16}(C_2H_3O)_2N_2$ [268°] (Bahrmann, *J. pr.* [2] 27, 295).—6. Amarine reacts with the *halogen compounds of the alkyls* to form substitution- and addition- compounds. Thus when amarine, methyl iodide, and ether are allowed to stand together in the cold, *methyl-amarine hydriodide*, $C_{21}H_{17}MeN_2,HI$, is formed. **Ammonia is without action upon this salt, but alcoholic potash liberates methylamarine [164°]. When amarine is heated with methyl iodide, a *dimethylamarine hydriodide*, $C_{21}H_{16}Me_2N_2,HI$, is** formed. Like the monomethyl compound it is not decomposed by ammonia; by treatment with alcoholic potash, dimethylamarine [146°] is obtained, and this base unites with hydriodic acid to form a hydriodide isomeric with the foregoing and differing from it in being decomposed by ammonia even in the cold (Claus a. Elbs, *B.* 13, 1418). Dimethylamarine and the other dialkyl-amarines do not combine with the halogen compounds of the alkyls.

Further derivatives of amarine.—*Ethyl-amarine*, $C_{21}H_{17}EtN_2$ [163°] (Claus a. Scherbel, *B.* 18, 3080); *diethylamarine*, $C_{21}H_{16}Et_2N_2$ [110°-115°] (Borodine, *A.* 110, 82).—*Benzyl-amarine*, $C_{21}H_{17}(C_7H_7)N_2$ [123°-124°]; *dibenzyl-amarine*, $C_{21}H_{16}(C_7H_7)_2N_2$ [139°-140°] (Claus a. Elbs, *B.* 13, 1418; Claus, *B.* 15, 2330; Claus a. Kohlstock, *B.* 18, 1819).—*Ethylbenzylamarine*, $C_{21}H_{16}Et(C_7H_7)N_2$ [135°] (C. a. K.).—*Hydro-methylbenzylamarine*, $C_{21}H_{18}Me(C_7H_7)N_2O$ [208°]; *hydrotrimethylamarine*, $C_{21}H_{17}Me_3N_2O$ [158°] (Claus, *B.* 15, 2326). — Other derivatives: $C_{21}H_{16}N_2(C_7H_5O).OEt$; $C_{21}H_{16}N_2(CO_2Et)_2$; and $C_{21}H_{16}N_2(CO_2Et)(CONHEt)$ (Bahrmann, *J. pr.* [2] 27, 295).—*Amarine-silver*, $C_{21}H_{17}AgN_2$ (Claus a. Elbs, *B.* 16, 1272); *diamarine silver nitrate*, $(C_{21}H_{18}N_2)_2,AgNO_3$ aq [218°] (C. a. K.).

When amarine silver is mixed with one molecular proportion of an alkyl-halogen compound (the latter diluted with benzene) and allowed to stand in the cold, a double compound of amarine-silver with the alkyl-halogen is obtained. At the same time a small quantity of monalkyl-amarine is formed from the double compound by elimination of silver iodide. In this way the following compounds have been prepared (Claus a. Scherbel, *B.* 18, 3077): *amarine-silver methylo-iodide*, $C_{21}H_{17}AgN_2,CH_3I$ [173°]; *amarine-silver ethylo-iodide*, $C_{21}H_{17}AgN_2,C_2H_5I$ [115°]; *amarine-silver isopropylo-bromide*, $C_{21}H_{17}AgN_2,C_3H_7Br$, [140°]; and finally *amarine-silver benzylo-chloride*, $C_{21}H_{17}AgN_2,C_7H_7Cl$, [250°]. When amarine-silver is treated with benzoyl chloride it yields *benzoyl-amarine*, $C_{21}H_{17}(C_7H_5O)N_2$, [180°], which forms salts with acids and also unites with benzoyl chloride to form *benzoyl-amarine benzoyl chloride*, $C_{21}H_{17}(C_7H_5O)N_2,C_7H_5OCl$, [312°], and with benzyl chloride to form *benzoyl-amarine benzylo-chloride*, $C_{21}H_{17}(C_7H_5O)N_2,C_7H_7Cl$ [351°], which latter is isomeric with *benzyl-amarine benzoyl chloride*, $C_{21}H_{17}(C_7H_7)N_2,C_7H_5OCl$, [340°-350°], obtained by the action of benzoyl chloride upon benzyl-amarine. The bases corresponding with these two chlorides are also isomeric. Benzoyl-amarine also unites with methyl iodide and with ethyl iodide to form additive compounds melting at 318° and 354° respectively (C. a. S.).

3. **Lophine** $C_{21}H_{16}N_2$ = 

Triphenylglyoxaline (Japp a. Robinson, *C. J.* 41, 323). [275°].

Formation.—1. By the destructive distillation of hydrobenzamide (Laurent, *A. Ch.* 19, 369), of amarine (Fownes, *T.* 1845, 263), or of tribenzylamine (Brunner, *A.* 151, 135). By the limited oxidation of amarine with chromic

acid (E. Fischer a. Troschke, *B.* 13, 706).—3. By passing ammonia into a warm alcoholic solution of a mixture of benzil and benzoic aldehyde:

$$\begin{matrix} C_6H_5.CO \\ C_6H_5.CO \end{matrix} + C_6H_5.CHO + 2NH_3 =$$

$$\begin{matrix} C_6H_5.C.NH \\ C_6H_5.C{-}N \end{matrix}\!\!>\!C.C_6H_5 + 3H_2O$$

(Radziszewski, *B.* 15, 1493; *cf.* Japp, *B.* 15, 2410).—4. By heating together *p*-oxybenzoic aldehyde, benzil, and ammonia, *p*-oxy-lophine, $C_{21}H_{15}(OH)N_2$, is formed (*v.* BENZIL, AMMONIA-DERIVATIVES OF, p. 466); and this, by distillation with zinc-dust, is converted into lophine (Japp a. Robinson, *C. J.* 41, 323).—5. By warming cyanphenine, $C_{21}H_{15}N_3$, with acetic acid and zinc dust, or by distilling it with potash and iron filings, it is converted into lophine and ammonia: $C_{21}H_{15}N_3 + 2H_2 = C_{21}H_{16}N_2 + NH_3$ (Radziszewski).

Preparation.—Hydrobenzamide is heated in a retort until the more volatile products of its decomposition—hydrogen, ammonia, and toluene—have been given off. The residue, which can only be distilled at a high temperature, is treated with ether, and then dissolved in glacial acetic acid. From this solution water precipitates lophine, which is finally purified by recrystallising it from boiling alcohol (Radziszewski, *B.* 10, 70).

Properties.—Crystallises in very slender, colourless silky needles [275°] (Radziszewski). Distils without decomposition at a high temperature. The vapour-density agrees with the formula $C_{21}H_{16}N_2$ (Fischer a. Troschke). Insol. water, sl. sol. alcohol and ether. Its solution in alcoholic potash phosphoresces when air is admitted, owing to a process of oxidation, in which the lophine is slowly converted into benzoic acid and ammonia (Radziszewski). Feebly basic: the salts are partially decomposed by water, in which they are for the most part insoluble; but they may be crystallised from alcohol.

Salts.—(Laurent, *A. Ch.* 19, 369; Atkinson a. Gössmann, *A.* 97, 283; Brunner, *A.* 151, 135). $C_{21}H_{16}N_2,HCl\frac{1}{2}aq$: obtained by adding hydrochloric acid to an alcoholic solution of lophine. According to Laurent and Brunner this salt is anhydrous.—$C_{21}H_{16}N_2,2HCl$: formed by the action of gaseous hydrochloric acid upon lophine.—$(C_{21}H_{16}N_2,HCl)_2,PtCl_4$: rhombic plates. Contains $5H_2O$ (Brunner). — $C_{21}H_{16}N_2,HI$. — $C_{21}H_{16}N_2,HNO_3$.—With silver nitrate it gives rise to: $C_{21}H_{16}N_2,AgNO_3$; $2C_{21}H_{16}N_2,AgNO_3$; and $2C_{21}H_{16}N_2,3AgNO_3$ (A. a. G.).

Reactions.—1. Oxidation with *chromic acid* in acetic acid solution converts lophine into a mixture of benzamide and dibenzamide:

$$C_{21}H_{16}N_2 + H_2O + O_2 =$$
$$C_6H_5.CONH_2 + (C_6H_5.CO)_2NH$$

(Fischer a. Troschke).—2. By the action of *bromine* upon lophine hydrobromide, an unstable perbromide of the formula, $C_{21}H_{16}N_2Br_6, HBr$(?), is obtained (F. a. T.).—3. *Nitric acid* yields, according to temperature and concentration, either *dinitrolophine*, $C_{21}H_{14}(NO_2)_2N_2$, or *trinitrolophine* $C_{21}H_{13}(NO_2)_3N_2$ (Laurent; Ekmann, *A.* 112, 161).—4. Heated with concentrated *sulphuric acid* to 160°-170° lophine is converted into *lophine-disulphonic acid*, $C_{21}H_{14}N_2(SO_3H)_2$ (F. a. T.).—5. With *ethyl iodide* at 100° it yields lophine hydriodide and *diethyllophinium iodide*, $C_{21}H_{15}EtN_2,EtI$; and this latter compound, by treatment with moist silver oxide yields the corresponding base (Kühn, *A.* 122, 326).

ISOMERIDE OF LOPHINE.—According to Kühn (*A.* 122, 313) an isomeride of lophine, $C_{21}H_{16}N_2\frac{1}{2}aq$, is obtained, together with ordinary lophine, by saturating hydrobenzamide with gaseous HCl, and heating the mixture to 230°. Needles [170°]. v. sol. boiling alcohol. Forms salts.

AZOBENZOILIDE, $C_{42}H_{33}N_3$(?) (Laurent, *A. Ch.* [3] 1, 306) and DIBENZOYLIMIDE, $C_{14}H_{13}NO$ (Robson, *C. J.* 4, 225), are also compounds which are stated to have been obtained by the action of ammonia upon benzoic aldehyde. They have been very little studied.

BENZOIC ALDEHYDE, HYDROCYANIC ACID, AND AMMONIA.—A number of compounds are obtained when ammonia acts upon benzoic aldehyde containing hydrocyanic acid. Some of these are, however, more readily prepared from the hydrocyanides of hydrobenzamide (*q. v.*) and have therefore been described under that head.—1. *Benzoylazotide*, $C_{15}H_{12}N_2$. Formed along with other products when a mixture of benzoic aldehyde, hydrocyanic acid, and ammonia is allowed to stand for some weeks (Laurent, *A. Ch.* [2] 66, 180; *vide supra*, 'Hydrobenzamide'). Crystalline powder, consisting of minute rhombic prisms, sl. sol. boiling alcohol. By destructive distillation it yields *amarone*, $C_{14}H_{11}N$, together with lophine and other products. Amarone forms colourless needles [233°], sl. sol. boiling alcohol (Laurent, *Revue Scient.* 18, 207).—2. *Azobenzoyl*, $C_{22}H_{16}N_2$, is formed according to the equation:

$$3C_7H_6O + HCN + NH_3 = C_{22}H_{16}N_2 + 3H_2O$$

(Beilstein a. Reinecke, *A.* 136, 175). White crystalline powder, insol. water, v. sol. ether. When warmed with alcohol and hydrochloric acid it is decomposed into HCN, amarine, and a base of the formula $C_{14}H_{16}N_2$, which latter crystallises in laminæ, melting at 122° (Müller a. Limpricht, *A.* 111, 140).—3. *Benzhydramide*, $C_{22}H_{18}N_2O$, is formed, along with the foregoing, from the same generating substances according to the equation: $3C_7H_6O + HCN + NH_3 = C_{22}H_{18}N_2O + 2H_2O$, and differs from it by containing the elements of a molecule of water more. Microscopic crystals. Sl. sol. alcohol, v. sol. ether (Laurent, *A. Ch.* [2] 66, 180; Laurent a. Gerhardt, *A.* 76, 302).

BENZOIC ALDEHYDE, AMMONIA, AND SULPHURETTED HYDROGEN.—1. Benzoic aldehyde and ammonium sulphide, if mixed and allowed to stand for some weeks, yield thio-benzaldin

$$3C_7H_6O + 2H_2S + NH_3 = C_{21}H_{19}NS_2 + 3H_2O$$

(Laurent, *A. Ch.* [3] 1, 291; also [3] 36, 342). Deposited from ether in monoclinic crystals [125°]. When boiled with alcohol it gradually evolves sulphuretted hydrogen.—2. By the action of ammonium sulphide upon crude oil of bitter almonds Laurent obtained a compound $C_{42}H_{36}N_4S_3$ (?).

Benzoic aldehyde slowly reacts in the cold with CS_2 and NH_3 to form a compound, $C_{15}H_{14}N_2S_2$ (Quadrat, *A.* 71, 13). The same substance is formed when benzoic aldehyde is mixed with ammonium thio-carbamate: $2C_7H_6O + CS_2 + 2NH_3 = C_{15}H_{14}N_2S_2 + 2H_2O$ (Mul-

der, *A.* 168, 238). Prismatic crystals, melting with decomposition at 100°. Cannot be dissolved in alcohol or ether without decomposition. The compound may be regarded as *di-benzylidene-ammonium dithio-carbamate*, $NH_2.CS.S.N(CH.C_6H_5)''_2$. F. R. J.

BENZOIC ALDEHYDE CARBOXYLIC ACID v. ALDEHYDO-BENZOIC ACID.

BENZOIC ALDEHYDE GREEN v. *Tetra*-METHYL-DIAMIDO-TRIPHENYL-CARBINOL.

BENZOIC ANHYDRIDE $C_{14}H_{10}O_3$ *i.e.* $(C_6H_5.CO)_2O$. *Benzoyl oxide.* Mol. w. 226. [42°]. (360° i.V.). S.G. (liquid) ^{22} 1·227. H.F. 104,815 (Stohmann, *J. pr.* [2] 36, 3).

Formation.—1. From BzCl and NaOBz, BaO, $H_2C_2O_4$, or $K_2C_2O_4$; or from NaOBz by the action of PCl_3, $POCl_3$, or S_2Cl_2 (Gerhardt, *A. Ch.* [3] 37, 299; Wunder, *J. pr.* 61, 498; Heintz, *P.* 92, 458; Gal, *A.* 128, 127; Anschütz, *B.* 10, 1882).—2. From benzotrichloride (1 pt.) and H_2SO_4 (3 pts. of 95·4 p.c.) (Jenssen, *B.* 12, 1495).—3. By the action of the dry nitrates (6 mols.) of Pb, Ag, Hg, Cu, or Zn upon benzoyl chloride (1 mol.) (*q. v.*) (Lachowicz, *B.* 18, 2990).

Properties.—Trimetric prisms, insol. water, m. sol. alcohol and ether. Slowly converted into benzoic acid by boiling water, more rapidly by alkalis. Hot NH_3Aq forms benzamide and ammonium benzoate. Combines with bromine (1 mol.). Gaseous HCl forms BzCl and HOBz.

Mixed Anhydrides.—Mixed anhydrides of the form BzOR are formed by the action of benzoyl chloride on the alkaline salts of various acids, or by the action of various alkoyl chlorides on sodium benzoate. They are generally decomposed by heat into a mixture of two anhydrides; and by water, more rapidly by alkalis, into two acids.

Benzo-acetic anhydride Ac.O.Bz v. ACETO-BENZOIC OXIDE, p. 17.

Benzo-isovaleric anhydride $Bz.O.C_5H_9O$. Oil (Chiozza, *A.* 84, 108).

Benzo-heptoic anhydride $Bz.O.C_7H_{13}O$. Oil. S.G. ^{11} 1·013 (Chiozza a. Malerba, *A.* 91, 102).

Benzo-pelargonic anhydride $BzO.C_9H_{17}O$. Oil (Chiozza, *A. Ch.* [3] 39, 209).

Benzo-myristic anhydride $BzO.C_{14}H_{27}O$. [38°].

Benzo-stearic anhydride $BzO.C_{18}H_{35}O$. [70°] (C. a. M.).

Benzo-angelic anhydride $BzO.C_5H_7O$. (C.). Oil.

Benzo-cinnamic anhydride $Bz.O.C_9H_7O$. Oil. S.G. ^{23} 1·184.

Benzo-cuminic anhydride $Bz.O.C_{10}H_{11}O$. Oil. S.G. ^{23} 1·115.

BENZOIC BROMIDE v. BENZOYL BROMIDE.

BENZOIC CHLORIDE v. BENZOYL CHLORIDE.

BENZOIC CYANIDE v. BENZOYL CYANIDE.

BENZOÏCIN v. *Tri-benzoyl*-GLYCERIN.

BENZOIC OXIDE v. BENZOIC ANHYDRIDE.

BENZOIC PEROXIDE v. BENZOYL PEROXIDE.

BENZOIN $C_{14}H_{12}O_2 = C_6H_5.CH(OH).CO.C_6H_5$. *Phenyl-benzoyl-carbinol.* [137°]. First prepared by Stange (*R. P.* 16, 93), and almost simultaneously by Robiquet (*A. Ch.* [2] 21, 254), by acting with a solution of potassium hydroxide or barium hydroxide upon crude oil of bitter almonds containing HCN.

Formation.—1. By partial oxidation of hydro-benzoïn, $C_6H_5.CH(OH).CH(OH).C_6H_5$ (Zinin, *A.* 123, 128).—2. By treating benzil $C_6H_5.CO.CO.C_6H_5$ with zinc and alcoholic hydrochloric acid (Z., *A.* 119, 177), with acetic acid and iron filings, or with K_2S.

Preparation.—200 g. of pure benzoic aldehyde are heated for a short time with a solution of 20 g. of KCN in 800 g. of 50 p.c. alcohol, and the liquid allowed to cool. Benzoïn separates and is removed by filtration. The filtrate, on heating with more KCN, yields a fresh quantity of benzoïn (Zincke, *A.* 198, 151). Two mols. of benzoic aldehyde unite to form 1 mol. of benzoïn: $2C_6H_5.CHO = C_6H_5.CH(OH).CO.C_6H_5$. The action of the KCN is not understood.

Properties.—Colourless, lustrous, six-sided prisms. Sl. sol. boiling water. V. sol. hot alcohol; sl. sol. in cold. Conc. H_2SO_4 dissolves it with a violet colour.

Reactions.—1. Partially decomposed by *distillation*. Repeated distillation breaks it up for the most part into 2 mols. of benzoic aldehyde; a smaller portion yields benzil and deoxybenzoïn: $2C_{14}H_{12}O_2 = C_{14}H_{10}O_2 + C_{14}H_{12}O + H_2O$ (Zinin, *B.* 6, 1207).—2. Treated in alcoholic solution with *zinc and hydrochloric acid* it is converted into deoxybenzoïn (Zinin, *A.* 126, 218); at the same time deoxybenzoïn-pinacone, $C_{28}H_{24}(OH)_2$, and hydrobenzoïn are formed (Goldenberg, *A.* 174, 332). *Sodium amalgam* reduces it to hydrobenzoïn. Heating with conc. *hydriodic acid* for some hours to 130° converts it into dibenzyl $C_{14}H_{14}$ (Goldenberg). By distillation with *zinc-dust* it yields stilbene, $C_{14}H_{12}$, together with an oily hydrocarbon isomeric with stilbene (Jena a. Limpricht, *A.* 155, 90).—3. *Nitric acid* oxidises it to benzil (Zinin); but *chromic acid*, or *potassium permanganate*, converts it into benzaldehyde and benzoic acid (Zincke, *B.* 4, 839). It reduces *Fehling's solution* in the cold, a property common to all compounds containing the group CO.CH(OH) (E. Fischer, *A.* 211, 215).—4. Fusion with *caustic potash* converts it into benzoic acid with evolution of hydrogen (Liebig a. Wöhler, *A.* 3, 276). When distilled with *soda-lime*, the benzoate which is first formed is decomposed by the excess of soda-lime, and benzene is obtained (Jena a. Limpricht). The action of *alcoholic potash* is complex: when benzoïn and alcoholic potash are heated with access of air, benzoic acid, a small quantity of benzilic acid ($C_{14}H_{12}O_3$), benzoïn ether ($C_{28}H_{22}O_3$ [157°]), and a compound $C_{30}H_{24}O_4$ (to which Limpricht a. Schwanert gave the name ethyl-dibenzoïn, assigning to it the formula $C_{30}H_{26}O_4$) are formed—this last, however, is produced from benzil generated by the air-oxidation of the benzoïn (v. BENZIL). If the benzoïn is heated with alcoholic potash in a sealed tube at 100° the products are benzoic acid, hydrobenzoïn, and ethylbenzilic acid ($C_{16}H_{16}O_3$). With very concentrated alcoholic potash at 160° benzoïn yields benzoic acid, stilbene, a compound $C_{28}H_{20}O_2$ and a small quantity of ethyl-benzilic acid. By heating benzoïn with a solution of sodium ethylate in alcohol, *ethyl-benzoïn*, $C_{14}H_{11}O_2.C_2H_5$ [95°], is formed, together with the various products already mentioned. Prisms, with a vitreous lustre, v. sol. alcohol (Jena a. Limpricht, *A.* 155, 89; Limpricht a. Schwanert, *B.* 4, 336; Japp a. Owens, *C. J.* 47, 90).—5. *Chlorine* acts like nitric acid, con-

verting benzoïn into benzil (Laurent, *A. Ch.* [2] 59, 401).—6. When heated with fuming *hydrochloric acid* at 130° for 6 or 8 hours it yields *lepidene*, $C_{28}H_{20}O$ (*q. v.*), benzil, and a thick yellow oil (Zinin, *J. pr.* 101, 160).—7. When boiled with dilute *sulphuric acid* it parts with the elements of water, yielding oxylepidene:— $2C_{14}H_{12}O_2 = C_{28}H_{20}O_2 + 2H_2O$ (Limpricht a. Schwanert, *B.* 4, 335). Concentrated sulphuric acid converts it into benzil (Zinin).—8. Heated with alcoholic *ammonia* for some hours at 100° in sealed tubes it yields *benzoïnam*, $C_{28}H_{21}N_2O$ (silky needles, v. sl. sol. alcohol, melting with decomposition), *benzoïnidam*, $C_{28}H_{23}NO_2$? [199°] (granular crystals, sl. sol. alcohol), and *tetra-phenyl-azine*,

$$\begin{array}{ccc} C_6H_5.C & -N- & C.C_6H_5 \\ \Vert & | & \Vert \\ C_6H_5.C & -N- & C.C_6H_5 \end{array}$$

[246°], together with some lophine, $C_{21}H_{16}N_2$. Tetra-phenyl-azine is best prepared by heating benzoïn with ammonium acetate until the salt is volatilised, dissolving the product in the strongest alcoholic hydrochloric acid, and ppg. with alcohol. V. sl. sol. alcohol, v. sol. alcoholic hydrochloric acid, v. sol. boiling benzene, sol. with blood-red colour in cold conc. H_2SO_4. Sublimes without decomposition. Heating with soda-lime converts it into *tetraphenylene-azine* $C_{28}H_{18}N_2$ (Laurent, *A. Ch.* [2] 66, 181; Erdmann, *A.* 135, 181; Japp a. Wilson, *C. J.* 1886, 825; Japp a. Burton, *C. J.* 1886, 843; 1887, 98).—9. Benzoïn reacts with the *primary amines of the benzenoid series*, when heated with them to 200°, eliminating 1 mol. of water and generating feebly basic compounds which by boiling with acids are decomposed into their generating substances. *Anilbenzoïn* $C_6H_5.CH(OH).C(N.C_6H_5).C_6H_5$ [99°], from aniline and benzoïn, forms yellowish needles, v. sol. most organic menstrua. Yields with nitrous acid *nitroso-anilbenzoïn* $C_6H_5.CH(OH).C(N.C_6H_4.NO).C_6H_5$ [140°], with acetic anhydride a *monacetyl-derivative* [153°], and with bromine a *monobromo-derivative* [168°]. Sodium amalgam reduces anilbenzoïn in alcoholic solution to *hydrobenzoïn-anilide* $C_6H_5.CH(OH).CH(NH.C_6H_5)C_6H_5$ [119°], which forms with sulphuric acid a salt not decomposed by boiling with the dilute acid.—*p-Tolilbenzoïn* $C_6H_5.CH(OH).C(N.C_6H_4.CH_3).C_6H_5$ [144°] resembles in its properties and its behaviour towards reagents the aniline compound. It yields with nitric acid a mono-nitro-derivative [125°] and a di-nitro-derivative [195°].—*β-Naphthilbenzoïn* [130°] also resembles the aniline compound (Voigt, *J. pr.* 34, 1).—10. Benzoïn reacts with *hydroxylamine* and with *phenyl-hydrazine*.—*Benzoïn-oxim*, $C_6H_5.CH(OH).C(N.OH).C_6H_5$ [151°-152°]. An alcoholic solution of benzoïn is mixed with an aqueous solution of hydroxylamine and allowed to stand for a week. Microscopic prisms, soluble in benzene (Wittenberg a. V. Meyer, *B.* 16, 504).—*Benzoïn-phenylhydrazide*, $C_6H_5.CH(OH).C(N_2H.C_6H_5).C_6H_5$ [155°]. Benzoïn and phenylhydrazine, together with a little alcohol, are heated at 100°. Needles, sol. benzene (Pickel, *A.* 232, 229).—11. By heating with *acid-chlorides* the hydroxylic hydrogen of benzoïn may be replaced by acid radicles to form ethereal salts. *Benzoïn acetate*, $C_{14}H_{11}(C_2H_3O)O_2$ [75°]. From benzoïn and acetyl chloride. Monoclinic prisms or tables, v. sol. ether and alcohol (Zinin, *A.* 104, 120; Jena a. Limpricht, *A.* 155, 92).—*Benzoïn benzoate*, $C_{14}H_{11}(C_7H_5O)O_2$ [125°]. By warming benzoïn with benzoyl chloride. Slender needles. Sol. hot alcohol. Yields a mono-nitro-compound [137°] (Zinin).—*Benzoïn succinate*, $(C_{14}H_{11}O_2)_2C_4H_4O_2$ [129°]. By heating benzoïn with succinyl chloride to 100°. Leaflets from alcohol. Sol. also in ether and CS_2 (Lukanin, *B.* 5, 331).—12. When benzoïn is heated with *hydrocyanic acid* and alcohol to 200° the process of its formation is reversed and it is broken up into benzoic aldehyde. A part of the benzoic aldehyde undergoes a further change, yielding amongst other products ethylic benzoate (Michael a. Palmer, *Am.* 7, 192).—13. *Phenyl cyanate* forms Ph.CH(O.CONPhH).CO.Ph [163°] (Gumpert, *J. pr.* [2] 32, 280). F. R. J.

BENZOÏN, GUM. A resin which flows from the bark of *Styrax benzoïn*, a tree growing in Sumatra, Borneo, Java, and Siam. Gum benzoin contains, besides various resins, benzoic acid and, frequently, cinnamic acid. Siamese and Palembang benzoins are free from cinnamic acid. Potash fusion produces benzoic, *p*-oxybenzoic, and protocatechuic acids, and pyrocatechin. Distillation with zinc-dust gives toluene and a little *o*-xylene, naphthalene, and methyl-naphthalene.

References.—Unverdorben, *P.* 8, 397; Van der Vliet, *A.* 34, 177; Kopp, *C. R.* 19, 1269; Kolbe a. Lautemann, *A.* 115, 113; 119, 136; Deville, *A. Ch.* [3] 3, 192; Ashoff, *J.* 1861, 400; Wiesner, *J.* 1872, 1060; Theegarten, *J.* 1874, 922; Ciamician, *B.* 11, 274; Saalfeld, *A. Ch.* [3] 16, 280.

BENZOÏN DI-*p*-CARBOXYLIC ACID $C_{16}H_{12}O_6$ *i.e.* $C_6H_4(CO_2H).CH(OH).CO.C_6H_4(CO_2H)$. Formed by oxidation of di-*p*-aldehydo-benzoïn with $KMnO_4$. Short felted needles. Sublimable. Infusible. Ag_2A''. *Di-methyl ether* Me_2A'': [126°] (Oppenheimer, *B.* 19, 1816).

BENZOLEÏC ACID $C_7H_{10}O_2$ *Hydrobenzoic acid*. Formed, together with benzyl alcohol, by the action of sodium amalgam on an aqueous solution of benzoïc acid kept acid by HCl (Hermann, *A.* 132, 75; Otto, *A.* 134, 303). Oil, smelling of valeric acid, heavier than water, v. sol. alcohol and ether.—EtA': oil.

BENZOLINE. A mixture of paraffins (hexane, heptane, octane) boiling between 70° and 100° obtained by distilling petroleum or paraffin oil. The mixture is also called petroleum spirit or ligroïn.

BENZOLON. Identical with lophine (*v.* BENZIL).

BENZODIMETHYLANILINE *v.* DIMETHYL-AMIDO-BENZOPHENONE.

***m*-BENZO-DI-METHYL-DI-FURFURANE.** $C_{12}H_{10}O_2$ *i.e.*

$$HC\overset{(1)}{\underset{(2)}{<}}{}^{CMe}_{O}{>}C_6H_2{<}^{CMe}_{O}\overset{(5)}{\underset{(6\ or\ 4)}{>}}CH.$$

[c. 27°]. (270° at 720 mm.). Obtained by evaporating (*β*)-benzo-di-methyl-di-furfurane-di-carboxylic ether $C_6H_2\left({<}^{CMe}_{O}{>}C.CO_2Et\right)_2$ with alcoholic KOH and lime, and dry distillation. Prisms. By warming with conc. H_2SO_4 a pure

blue colouration is produced (Hantzsch, *B.* 19, 2938; 20, 1337).

p-**Benzo-di-methyl-di-furfurane** $C_6H_2\Big(<\begin{smallmatrix}CMe\\O\end{smallmatrix}>CH\Big)_2$. [108°]. Obtained by heating the potassium salt of the di-carboxylic acid with lime. Large pearly tables with bluish fluorescence. V. sol. alcohol, ether, etc. (Nuth, *B.* 20, 1337).

Benzo-tri-methyl-tri-furfurane $C_{15}H_{12}O_3$ *i.e.* $C_6\Big(<\begin{smallmatrix}CMe\\O\end{smallmatrix}>CH\Big)_3$. [115°-120°]. Needles. Very soluble in ordinary solvents. Formed by evaporating the tri-carboxylic ether $C_6\Big(<\begin{smallmatrix}CMe\\O\end{smallmatrix}>C.CO_2Et\Big)_3$ with alcoholic KOH and lime, and dry distillation (Lang, *B.* 19, 2936).

***o*-BENZO-DI-METHYL-DI-FURFURANE DI-CARBOXYLIC ACID**

$C_6H_2\Big(<\begin{smallmatrix}CMe\\O\end{smallmatrix}>C.CO_2H\Big)_2$. Obtained by saponification of the ethyl-ether which is formed by dissolving in conc. H_2SO_4 the product of the action of chloracetoacetic ether (2 mols.) upon di-sodium pyrocatechin (1 mol.). Amorphous solid.—BaA″ 2aq.

Di-ethyl ether Et_2A'': [155°]; short prisms (from alcohol), or long white needles (from ether) (Nuth, *B.* 20, 1337).

(α)-*m*-**Benzo-di-methyl-di-furfurane di-carboxylic acid** $C_{14}H_{10}O_6$ *i.e.*

$HO_2C.C\overset{(1)}{\underset{(2)}{<\begin{smallmatrix}CMe\\O\end{smallmatrix}>}}C_6H_2\overset{(5)}{\underset{(4\text{ or }6)}{<\begin{smallmatrix}CMe\\O\end{smallmatrix}>}}C.CO_2H$. [Far above 310°]. Formed by saponification of the di-ethyl-ether. This ether is obtained, together with a much larger quantity of the (β)-isomeride by the action of chloro-acetoacetic ether upon di-sodium resorcin $C_6H_4(ONa)_2$ in presence of alcohol, extracting with benzene, dissolving the undissolved portion in conc. H_2SO_4, pouring into water, and extracting with ether; when the ethereal solution is mixed with hot alcohol and allowed to cool the (α)-ether crystallises out, whilst the (β)-ether remains in solution. The two ethers are also formed (the α in very small quantity) by heating oxy-methyl-coumarilic ether $C_6H_3\overset{(4)}{(OH)}\overset{(1)}{\underset{(2)}{<\begin{smallmatrix}CMe\\O\end{smallmatrix}>}}C.CO_2Et$ with chloro-aceto-acetic ether and alcoholic NaOEt, and dissolving the product in H_2SO_4. The acid is a white microcrystalline solid. Scarcely soluble in water, more readily in alcohol. The salts of the heavy metals are all sparingly soluble. Warm H_2SO_4 produces a pure blue colouration.

Di-ethyl ether $A''Et_2$: [186°]; needles; sl. sol. alcohol (Hantzsch, *B.* 19, 2930).

(β)-*m*-**Benzo-di-methyl-di-furfurane-di-carboxylic acid** $C_{14}H_{10}O_6$ *i.e.*

$HO_2C.C\overset{(1)}{\underset{(2)}{<\begin{smallmatrix}CMe\\O\end{smallmatrix}>}}C_6H_2\overset{(5)}{\underset{(6\text{ or }4)}{<\begin{smallmatrix}CMe\\O\end{smallmatrix}>}}C.CO_2H$. [Far above 310°]. Formed by saponification of its di-ethyl ether. Microcrystalline solid. Scarcely soluble in water, more easily in alcohol. Gives sparingly soluble pps. with the salts of the heavy metals. The acid and its ether give a pure blue colouration with warm H_2SO_4.

Di-ethyl ether $A''Et_2$: [141°]; small white needles; more soluble than the (β)-isomeride. Formed, together with a small quantity of the (β)-ether, by the action of chloro-acetacetic ether upon dry di-sodium resorcin, extraction with benzene, dissolving the residue in conc. H_2SO_4, pouring into water, and extracting with ether. Also by heating oxy-methyl-coumarilic ether $C_6H_3\overset{(4)}{(OH)}\overset{(1)}{\underset{(2)}{<\begin{smallmatrix}CMe\\O\end{smallmatrix}>}}C.CO_2Et$ with chloro-acetacetic ether and alcoholic NaOEt, and dissolving the product in H_2SO_4. By evaporation with alcoholic KOH and lime and dry distillation it yields (β)-benzo-di-methyl-di-furfurane $C_6H_2\Big(<\begin{smallmatrix}CMe\\O\end{smallmatrix}>CH\Big)_2$. (Hantzsch, *B.* 19, 2930).

p-**Benzo-di-methyl-di-furfurane di-carboxylic acid** $C_6H_2\Big(<\begin{smallmatrix}CMe\\O\end{smallmatrix}>C.CO_2H\Big)_2$. Obtained by saponification of its ethyl-ether which is formed by dissolving in conc. H_2SO_4 the product of the action of chloro-acetacetic ether (2 mols.) upon di-sodium hydroquinone (1 mol.). Amorphous solid (containing aq).

Salts.—Ag_2A'': white pp.—BaA″ 2aq: sl. sol. yellowish-white powder.

Ethyl ether Et_2A'': [150°]; glistening greenish plates; v. sl. sol. all solvents (Nuth, *B.* 20, 1334).

Benzo-tri-methyl-tri-furfurane-tri-carboxylic acid $C_{18}H_{12}O_9$ *i.e.* $C_6\Big(<\begin{smallmatrix}CMe\\O\end{smallmatrix}>C.CO_2H\Big)_3$. Formed by saponification of its ethyl ether which is obtained by treating dry powdered tri-sodium-phloroglucol (1 mol.) with chloro-acetacetic ether (3 mols.), dissolving the product in H_2SO_4 and pouring into water. Gelatinous pp. (containing aq). Scarcely soluble in alcohol and ether. Its salts are mostly insoluble and gelatinous. $Ba_3A'''_2$ 7aq: microcrystalline.

Ethyl ether Et_3A''': [c. 298°]; small white glistening needles; sl. sol. all solvents, most readily in chloroform (Lang, *B.* 19, 2935).

BENZONAPHTHONE *v.* NAPHTHOQUINONE.

BENZONAPHTHYL-THIAMIDE *v.* *Thiobenzoyl*-(α)-NAPHTHYLAMINE.

BENZONITRILE C_7H_5N *i.e.* $C_6H_5.CN$. Mol. w. 103. [−17°] (Hofmann). (190·5°). S.G. $\frac{0}{0}$ 1·023; $\frac{15}{}$ 1·008 (Kopp, *A.* 98, 373). S. 1 at 100°. S.V. 123·7 (Ramsay).

Formation.—1. By the dry distillation of ammonium benzoate (Fehling, *A.* 49, 91).—2. From benzamide by heating it alone or with CaO (Anschütz a. Schultz, *A.* 196, 48), BaO (Wöhler, *A.* 192, 362), P_2O_5 (Hofmann a. Buckton, *A.* 100, 155), PCl_5 (Hencke, *A.* 106, 276), or P_2S_5 (Henry, *B.* 2, 307).—3. By heating hippuric acid alone (Limpricht a. Uslar, *A.* 88, 133), or with $ZnCl_2$ (Gössmann, *A.* 100, 74).—4. By the action of BzCl or Bz_2O on benzamide.—5. By the action of BzCl on oxamide, on potassium sulphocyanide (Limpricht, *A.* 99, 117), or on potassium cyanate (Schiff, *A.* 101, 93).—6. By heating Bz_2O with potassium cyanate or sulphocyanide.—7. By the action of HgO on thiobenzamide.—8. By heating benzoic acid with sulphocyanide of lead (Krüss, *B.* 17, 1767), or of potassium (Letts, *B.* 5, 673).—9. From potassium benzoate and [illegible]

A. Ch. [3] 52, 200).—10. By distilling a mixture of aniline and oxalic acid (Hofmann, *C. R.* 64, 388).—11. Formed by distilling formanilide over zinc-dust; the yield is nearly 20 p.c. of the formanilide (Gasiorowski a. Merz, *B.* 17, 73; *B.* 18, 1001).—12. Formed together with sodium formate, by the action of dilute NaOH upon aniline di-chloro-acetate (Cech a. Schwebel, *C. C.* 1877, 134).—13. Formed by running an aqueous solution of diazobenzene chloride into a hot solution of $Cu_2(CN)_2$ (Sandmeyer, *B.* 17, 2653).—14. By heating tri-phenyl phosphate with potassium cyanide or ferrocyanide; the yield is 25 p.c. of the theoretical (Scrugham, *A.* 92, 318; Heim, *B.* 16, 1771).—15. By heating potassium benzene sulphonate with KCN (Merz, *Z.* 1868, 33).—16. From K_4FeCy_6 and chloro- or bromo-benzene at 400° (Merz a. Weith, *B.* 8, 918; 10, 749).—17. From iodo-benzene and AgCy (Merz a. Schelnberger, *B.* 8, 1630).—18. Together with terephthalonitrile, by passing a mixture of benzene and cyanogen through a red-hot tube (M. a. S.). — 19. By passing dimethylaniline through a red-hot tube (Nietzki, *B.* 10, 474).—20. By the action of CyCl on benzene in presence of aluminium chloride (Friedel a. Crafts, *Bl.* [2] 29, 2). —21. From bromo-benzene, Cy_3Cl_3, and Na (Klason, *J. pr.* [2] 35, 83).—22. By boiling phenyl thiocarbimide with finely divided Cu.—23. From phenyl carbamine by intramolecular change at 240° (Weith, *B.* 6, 213).—24. By the action of acetic anhydride on benzaldoxim (Lach, *B.* 17, 1571).

Properties.—Colourless oil, smelling of almonds; sinks in cold, but swims in hot water; miscible with alcohol and ether.

Reactions.—1. Cold *aqueous potash* has no action, but on boiling it forms NH_3 and KOBz; *dilute acids* act similarly.—2. Heating with *potassium* gives KCy, cyaphenine, $(C_6H_5)_3Cy_3$, and other bodies (Bingley, *Chem. Gaz.* 1854, 329; Hofmann, *B.* 1, 198). When the boiling alcoholic solution is treated with *sodium*, the greater part is saponified whilst a smaller portion undergoes reduction to benzylamine and to benzene (Bamberger a. Lodter, *B.* 20, 1709).—3. H_2S or *ammonium sulphide* forms thiobenzamide.—4. Zn and HCl in alcoholic solution form mono-, di-, and tri-benzylamine (Mendius, *A.* 121, 129; Spica, *G.* 10, 515).—5. Fuming H_2SO_4 forms, on heating, benzene sulphonic acid; at 20° it forms cyaphenine. Benzonitrile (10g.) cooled with ice and treated with fuming H_2SO_4 (7 g.) added slowly, forms dibenzamide $NHBz_2$ [148°], and 'benzimido-benzamide' $NHBz.C(NH).C_6H_5$ [106°], called by Pinner a. Klein 'benzimido-benzoate' and 'dibenzimido-oxide,' respectively. Dilute HCl converts the former into the latter (F. Gumpert, *J. pr.* [2] 30, 87; Pinner, *ibid.*, 125).—6. Boiled with *zinc ethyl* it gives off ethane (1 vol.) and an olefine (1 vol.) and forms a product, whence, by treatment first with alcohol, and then with aqueous HCl, cyaphenine (*q. v.*) and the hydrochloride of a base which crystallises in six-sided plates, $C_{16}H_{19}N_2Cl$, is formed. This body [257°] is readily soluble in alcohol, but sparingly so in water. Potash liberates the base as a colourless oil (Frankland a. Evans, *C. J.* 37, 565).—7. By exhaustive chlorination with $SbCl_5$ it yields penta-chloro-cyano-benzene $C_6Cl_5(CN)$ (Merz a. Weith, *B.* 16, 2885).—8. With methylal and H_2SO_4 it gives the benzoyl derivative of methylene diamine (*q. v.*).—9. With *diphenylamine hydrochloride* at 180° it forms di-phenyl-benzamidine; but at 240° it forms a Base $C_{19}H_{13}N$, [183°], thus: $C_6H_5C(NH)N(C_6H_5)_2 = NH_3 + C_{19}H_{13}N$. *Properties.*—Thick prisms (from benzene), containing benzene of crystallisation; yellow tablets (occasionally from benzene); long thin prisms (from alcohol). The tablets are monoclinic, a:b:c = ·5875:1:·5014, ∠ = 51° 23' (Bodewig). Soluble in benzene and ether, slightly in alcohol. Its alcoholic solution is neutral. Acetyl chloride does not act on it. **Salts**: B'HCl. Narrow red prisms. [Above 220°.]—$(B'HCl)_2PtCl_4$.

Combinations.—1. With **metallic chlorides.** — $(C_7H_5N)_2AuCl_3$. — $(C_7H_5N)_2PtCl_4$.— $(C_7H_5N)_2SnCl_4$.—$(C_7H_5N)_2TiCl_4$ (Henke, *A.* 106, 284).—2. With **halogens.** $C_6H_5.CBr:NBr$.— $(C_6H_5CN)_2Br_2$: needles (Engler, *A.* 133, 137).— 3. With **hydrogen chloride:** $C_7H_5N\,2HCl$ (Pinner a. Klein, *B.* 10, 1891; *cf.* Gerhardt, *Traité*, 4, 762). — 4. With **hydrogen bromide.** $C_7H_5N\,2HBr$. [70°] (Engler, *A.* 149, 307). — 5. With **alcohols.**—*Benzimido-ethyl ether*, $C_6H_5.C(OEt):NH$. The hydrochloride, B'HCl, is formed by passing dry HCl gas into a mixture of ethyl alcohol and benzonitrile, diluted with ether. Large glistening prisms; decomposes on heating to about 120° into ethyl chloride and benzamide (Pinner, *B.* 16, 1654). *Benzimido-isobutyl ether* $C_6H_5.C(OC_4H_9):NH$. The hydrochloride B'2HCl is formed by passing HCl into a cooled mixture of benzonitrile and isobutyl alcohol (Pinner a. Klein, *B.* 10, 1890); it gradually loses HCl becoming B'HCl, [135°].—$B'_2H_2PtCl_6$.—$B'H_2SO_4$. —6. With **acids.** — *Benzimido-acetate* $C_6H_5.C(OAc):NH$. [116°]. From benzimido-isobutyl ether and Ac_2O (Pinner a. Klein, *B.* 11, 9).—7. With **mercaptans.** — *Benzimido-ethyl thio-ether* $C_6H_5.C(SEt):NH$. From benzonitrile, mercaptan, and HCl, or from thiobenzamide and EtI (Bernthsen, *A.* 197, 348). Oil; decomposes readily into mercaptan and benzonitrile.—B'HCl. [188°]. — $B'_2H_2PtCl_6$.— B'HI. [142°]. *Benzimido-isoamyl thio-ether* $C_6H_5.C(SC_5H_{11}):NH$. The hydrochloride, B'HCl, is formed by passing HCl into a mixture of benzonitrile and isoamyl mercaptan (Pinner a. Klein, *B.* 11, 1825). The free base is an oil. *Benzimido-benzyl-thio-ether* $C_6H_5.C(SC_7H_7):NH$. Prepared like the ethyl ether.—B'HCl [181°].

Derivatives of Benzonitrile are described as Bromo-, Nitro- &c. benzonitrile.

BENZO-PHENOL *v.* Oxy-benzophenone.

BENZOPHENONE $C_{13}H_{10}O$ *i.e.* $C_6H_5.CO.C_6H_5$. *Di-phenyl-ketone.* Mol. w. 182. [48°]. (305° i.V.).

Formation.—By the dry distillation of calcium benzoate (Peligot, *A.* 12, 41; Chancel, *A.* 72, 279).—2. From BzCl and $HgPh_2$ (Otto, *B.* 3, 197).—3. From BzCl and benzene in presence of Al_2Cl_6.—4. From benzoic acid, benzene, and P_2O_5 at 190° (Kollarits a. Merz, *B.* 6, 446, 538). 5. From benzene, $COCl_2$, and Al_2Cl_6 (Friedel, Crafts, a. Ador, *C. R.* 85, 673).—6. By oxidation of di-phenyl-methane (Zincke, *A.* 159, 377).

Preparation.—From BzCl, C_6H_6, and Al_2Cl_6;

the yield is 70 p.c. of the calculated (Elbs, *J. pr.* [2] 35, 465).

Properties.—Prisms; insol. water, v. sol. alcohol and ether.

Reactions.—1. Reduced by HI to di-phenyl-methane (Graebe, *B.* 7, 1624).—2. Reduced by *zinc-dust* to di-phenyl-methane, tetra-phenyl-ethylene, and tetra-phenyl-ethane (Staedel, *A.* 194, 307).—3. *Potash-fusion* gives benzoic acid and benzene.—4. Reduced to di-phenyl-carbinol by *sodium-amalgam* or by heating with *alcoholic potash.*—5. *Ammonia* has no action.—6. Zn and alcoholic H_2SO_4 reduce it to benzpinacone and (α)- and (β)- benzpinacolin (Zincke a. Thörner, *B.* 11, 1396).—7. AcCl in presence of zinc-dust acts on an ethereal solution forming crystalline (α)- and (β)- benzpinacolin.—8. PCl_5 forms di-chloro-di-phenyl-methane.—9. Passage through a *red-hot tube* slightly decomposes it; the product contains benzene, di-phenyl, and *p*-di-phenyl-benzene, while gaseous carbonic oxide, hydrogen, and acetylene escape (Barbier a. Roux, *C. R.* 102, 1559).—10. When heated with ammonium formate at 200°-220° it yields the formyl derivative of di-phenyl-carbinyl-amine $(C_6H_5)_2CH.NH.CHO$ (Leuckart a. Bach, *B.* 19, 2129).—11. P_2S_5 at 100° forms $C_{26}H_{22}S_2$ [153°], crystallising in lustrous flat monoclinic needles. At 200° it turns deep blue (Japp a. Raschen, *C. J.* 49, 481).—12. P_2S_5 at 140° forms $C_{26}H_{20}P_2S_5$ [227°], crystallising in minute plates, insol. alcohol, sl. sol. hot benzene. On melting it turns deep blue. It is oxidised by CrO_3 in HOAc to benzophenone (J. a. R.).

Oxim $(C_6H_5)_2C:NOH$. *Di-phenyl-ketoxim.* [140°]. Prepared by boiling an alcoholic solution of benzophenone (30g.) with hydroxylamine hydrochloride (28g.) and a little HCl for a day (Beckmann, *B.* 19, 988; Janny, *B.* 15, 2782). Silky needles, v. sol. ether and acetone, m. sol. benzene and ligroïn, v. sl. sol. cold water. Sol. acids and alkalis. Resolved by acids into its constituents. By PCl_5 or $POCl_3$ it is converted into ω-chloro-benzylidene-aniline, $C_6H_5.N:CCl.C_6H_5$, produced by intramolecular change from $(C_6H_5)_2C:NCl$ (B.). By warming with conc. H_2SO_4 to 100° it is converted by similar isomeric change into benzanilide (Beckmann, *B.* 20, 1507). Salts.—$C_{13}H_{10}N(ONa)$: crystalline powder.—$C_{13}H_{10}N(OH).HCl$: white powder.

Methyl-oxim $C_{13}H_{10}N(OMe)$: [92°]; yellow crystals.

Ethyl-oxim $C_{13}H_{10}N(OEt)$: (276°-279°); fluid.

Benzyl-oxim $C_{13}H_{10}N(OC_7H_7)$: [56°]; white crystals.

Acetyl oxim $C_{13}H_{10}N(OAc)$: [55°]; white crystals (Spiegler, *B.* 17, 810; *M.* 5, 203).

Phenyl hydrazide $Ph_2C:N_2HPh$. [137°]. Got by boiling benzophenone with phenyl hydrazine and alcohol; or by heating the oxim with phenyl-hydrazine, N_2 and NH_3 being evolved. Needles (from alcohol). Insoluble in water, not very soluble in alcohol. Heated for some time with dilute (20 p.c.) HCl, it is resolved into benzophenone and phenyl hydrazine (Pickel, *A.* 232, 228; Fischer, *B.* 17, 576; Just, *B.* 19, 1206).

Isomeride of Benzophenone. [26°]. (305°). Sometimes formed in oxidising di-phenyl-methane or in distilling calcium acetate with calcium benzoate (Zincke, *A.* 159, 367). Readily changes into ordinary benzophenone.

Derivatives of benzophenone are described as Amido-, Bromo-, Chloro-, Cyano-, Nitro-, Oxy-, &c., Benzophenone, and as *Di*-phenylene-ketone oxide.

BENZOPHENONE-CARBOXYLIC ACID *v.* Benzoyl-benzoic acid.

BENZOPHENONE-DI-*p*-CARBOXYLIC ACID [4:1] $C_6H_4(CO_2H).CO.C_6H_4(CO_2H)$ [1:4]. Formed by boiling di-*p*-cyano-benzophenone with alcoholic KOH (Brömme, *B.* 20, 522). Also by the oxidation of di-tolyl-methane, or di-methyl-benzophenone, with chromic mixture (Weiler, *B.* 7, 1185; Ador a. Crafts, *B.* 10, 2173). Microscopic needles. Sublimes at a high temperature without melting. Sl. sol. alcohol, benzene, and ether. S. (hot water) = ·002. The NH_4 salt gives pps. with salts of Fe, Co, Cu, Ba, and Ca, but not with salts of Pb, Cr, Zn, Mg, and Ni.

Silver salt $A''Ag_2$, Ag_2O: insol. water.

Di-methyl ether $A''Me_2$: [138°]; large needles (B.). Ag_2A' (A. a. C.).

Benzophenone dicarboxylic acid $C_6H_5.CO.C_6H_3(CO_2H)_2$.

Benzoyl-isophthalic acid: [280°]. From benzyl-isoxylene and chromic mixture (Zincke, *B.* 9, 1762). Sl. sol. hot water and $CHCl_3$, v. sol. alcohol. Converted by Zn and HCl into the lactone of $C_6H_5.C(OH)H.C_6H_3(CO_2H)_2$.—Salts: CaA″aq.—BaA″aq.—Ag_2A''.

Methyl ether Me_2A''. [118°].

Ethyl ether Et_2A''. [95°].

Benzophenone dicarboxylic acid $C_6H_5.CO.C_6H_3(CO_2H)_2$. [1:2:5].

Benzoyl-terephthalic acid. [290°] (W.); [285°] (E.).

Formation.—1. By oxidising benzyl-cymene with chromic mixture (Weber, *J.* 1878, 402).—2. From benzoyl-*p*-xylene and HNO_3 (S. G. 1·15) at 170° (Elbs, *J. pr.* [2] 35, 479).—3. From phenyl *p*-cymyl ketone and dilute HNO_3.

Properties.—V. sl. sol. water, v. sol. alcohol. Reduced by Zn and HCl to

$C_6H_5.CH(OH).C_6H_3(CO_2H)_2$.—CaA″ aq.—BaA″ 5aq.—$Ag_2A''$.

Methyl ether Me_2A''. [101°]: needles.

Ethyl ether Et_2A''. [101°]: prisms.

Benzophenone tetra-carboxylic acid $C_6H_5.CO.C_6H(CO_2H)_4$. From benzoyl-iso-durene and $KMnO_4$ (Essner a. Gossin, *Bl.* [2] 42, 170).

BENZOPHENONE CHLORIDE is *exo*-Di-chloro-di-phenyl-methane (*q. v.*).

BENZOPHENONE OXIDE *v.* *Di*-phenylene-ketone oxide.

BENZOPHENONE SULPHONE $C_{13}H_8SO_3$ *i.e.* $SO_2<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>CO$. [187°]. From benzophenone and fuming H_2SO_4 (Beckmann, *B.* 6, 1112; 8, 992). V. sol. ether, sol. alkalis; converted by water at 190° into an isomeride (?) [175°].

BENZOPHENONE DI-SULPHONIC ACID $C_{13}H_8(SO_3H)_2O$. From benzophenone and fuming H_2SO_4 by warming (Staedel, *A.* 194, 314). Converted by potash fusion into phenol and *p*-oxy-benzoic acid.—BaA″.

Chloride $CO(C_6H_4SO_2Cl)_2$. [122°] (Beckmann, *B.* 8, 992).

BENZOPHENYL- *v.* Benzoyl-phenyl-.

BENZOPHOSPHINIC ACID is CARBOXY-BENZENE PHOSPHONIC ACID (*q. v.*).

BENZOPINACOLIN is BENZPINACOLIN (*q. v.*).

BENZOPINACONE is BENZPINACONE (*q. v.*).

BENZOQUINOL is HYDROQUINONE (*q. v.*).

BENZOQUINONE is QUINONE (*q. v.*).

BENZORESORCIN *v.* DIOXYBENZOPHENONE.

DI-BENZO-RESORCIN *v.* DIOXYPHENYLENE-DI-PHENYL-DI-KETONE.

BENZOSTILBINE is lophine (*v.* p. 474).

BENZO-SUCCINIC ACID *v.* BENZOYL-SUCCINIC ACID.

BENZOTHIAMIDE *v.* THIO-BENZAMIDE.

BENZO-TOLUIDINE *v.* PHENYL AMIDO-TOLYL KETONE.

BENZTROPEÏNE *v.* BENZOYL-TROPEÏNE.

BENZOXAMIDINE *v.* BENZAMIDOXIM.

BENZ-OXIMIDO-AMIDE *v.* BENZAMIDOXIM.

BENZ-OXIMIDO-ETHYL-ETHER $C_9H_{11}NO_2$ *i.e.* $C_6H_5.C(OEt):NOH$. Formed by the action of hydroxylamine hydrochloride on benz-imido-ether (*v.* BENZONITRILE), (Pinner, *B.* 17, 184). Colourless fluid. Decomposes on distillation.

BENZOXY- *v.* *Benzoyl*-OXY-.

BENZOXY-PROPIO-CARBOXYLIC ACID *v* CARBOXY-BENZOYL-PROPIONIC ACID.

BENZOYL. The radicle $C_6H_5.CO$. Benzoyl derivatives obtained by displacement of H in amidogen, imidogen, or hydroxyl, are described under the compounds from which they are thus derived.

Di-benzoyl is called BENZIL (*q. v.*).

BENZOYL-ACET-CARBOXYLIC ACID *v.* ACETOPHENONE DI-CARBOXYLIC ACID.

BENZOYL-ACETIC ACID $C_9H_8O_3$ *i.e.* $C_6H_5.CO.CH_2.CO_2H$. *Acetophenone ω-carboxylic acid.* [104°].

Formation.—1. From the ether by leaving it 24 hours with cold dilute KOH (3 per cent.), cooling to 0° and then adding dilute H_2SO_4. The acid is then ppd. as white flakes (Baeyer a. Perkin, *B.* 15, 2705; 16, 2128; W. H. Perkin, jun., *C. J.* 45, 176).—2. From phenyl propiolic acid and conc. H_2SO_4, the solution being poured upon ice.—3. From the ether by allowing it to stand for 14 days with 20 vols. of conc. H_2SO_4 and then pouring upon ice (Perkin, *C. J.* 47, 240).

Properties.—Minute needles, which polarise light (from benzene at 70° containing a little light petroleum). At 104° it melts, and gives off CO_2. Sl. sol. light petroleum, v. sol. alcohol, ether, hot benzene, and hot water. Fe_2Cl_6 colours its alcoholic or aqueous solutions reddish-violet.

Reaction.—1. *Heated* alone or with dilute H_2SO_4 it gives acetophenone and CO_2.—2. The ammonium salt gives with $AgNO_3$ a pp. of AgA'; with Fe_2Cl_6 a blackish-violet pp.; with $FeSO_4$ no pp.; with $CuSO_4$, a greenish-yellow pp.

Methyl ether MeA'. An oil prepared by the action of conc. H_2SO_4 on methyl phenyl-propiolate (W. H. Perkin, jun., a. Calman, *C. J.* 49, 154). Fe_2Cl_6 gives a violet colour in alcoholic solution. Sodium ethylate gives a white amorphous salt, $C_6H_5.CO.CHNa.CO_2Me$. This salt is v. sol. water and hot alcohol.

Ethyl ether. A'Et. (265°-270°) at 760 mm.; (230°-235°) at 200 mm.

Formation.—1. From phenyl-propiolic ether (100 g.) and H_2SO_4 (3000 g.) at 0°. After three hours the product is poured upon powdered ice, and the new body extracted with ether.—2. By heating diazo-acetic ether with benzoic aldehyde (Buchner a. Curtius, *B.* 18, 2371).—3. By heating EtONa (140 g.) with benzoic ether (300 g.) at 100°, mixing the product with acetic ether (350 g.) and heating for 15 hours at 100° (Claisen a. Lowman, *B.* 20, 651).—4. By the action of cold conc. H_2SO_4 upon (α)-bromo-cinnamic ether (Michael a. Browne, *B.* 19, 1392).

Properties.—Colourless oil. Partly decomposed when distilled. Sl. sol. water, sol. alcohol and ether.

Reactions.—1. The alcoholic solution gives with Fe_2Cl_6 a violet colour.—2. Boiled with *water*, or dilute H_2SO_4, it gives acetophenone, alcohol, and CO_2.—3. *Boiling* for 8 minutes produces dehydro-benzoyl-acetic acid (*q. v.*). Boiling for 30 minutes forms two isomerides $(C_9H_6O_2)_n$. One of these (n = 3 ?) crystallises in plates, [275°], m. sol. hot alcohol, v. sl. sol. benzene; sol. alcoholic NaOH but ppd. by CO_2. The second (n = 4 ?) is an acid, not being ppd. by CO_2 from its solution in alcoholic NaOH; conc. H_2SO_4 forms a yellow solution, turning violet when warmed (Perkin, jun., *C. J.* 47, 262).—4. $NaNO_2$ and H_2SO_4 added to the sodium derivative produce an oxim of benzoyl-glyoxylic ether, $Ph.CO.C(NOH).CO_2Et$ [121°], whence alkalis produce a substance $C_8H_5O_4$ [125°].

Metallic derivatives. $BzCHNaCO_2Et$. Got by adding NaOEt to alcoholic solution of the ether. Silky needles, turns brown in air; insol. ether. — $(C_{11}H_{11}O_3)_2Ba$. — $C_{11}H_{11}AgO_3$.— $(C_{11}H_{11}O_3)_2Cu$: pale green; soluble in aqueous NaOH. On boiling Cu_2O is ppd.

Nitrile v. BENZOYL-ACETONITRILE.

Benzylidene-benzoyl-acetic ether $C_6H_5.CH:CBz.CO_2Et$. [99°]. From benzoyl-acetic ether and benzoic aldehyde, either by passing HCl at 0° into the mixture, or by heating in a sealed tube (Perkin, jun., *C. J.* 47, 240). Monoclinic prisms: $a:b:c = 1{\cdot}2730:1:{\cdot}7460$; $\beta = 86° 36'$. Sol. hot methyl alcohol. Conc. H_2SO_4 forms a yellow solution, which becomes colourless on heating.

Benzylidene-di-benzoyl-di-acetic acid $(CO_2H.CHBz)_2CHPh$. [130°]. The ethers of this acid are formed by dropping diazo-acetic ethers (2 mols.) into benzoic aldehyde (3 mols.) at 170° (Buchner a. Curtius, *B.* 18, 2374). They dissolve in conc. H_2SO_4 forming rose-coloured solutions, which turn brown on warming. The acid and its ethers give off a smell of hyacinths when burnt.

Methyl ether [113°]: prisms.

Ethyl ether [103°]: tables; NaOEt added to its ethereal solution gives $(CO_2Et.CNaBz)_2CHPh$.

Di-benzoyl-acetic acid $CHBz_2.CO_2H$. [109°]. Formed by the action of BzCl on sodium benzoyl-acetic ether, and saponification of the product with KOH (Baeyer a. Perkin, jun., *B.* 16, 2133; *C. J.* 47, 240). Slender felted needles, sl. sol. cold alcohol and water, v. sol. ether; sol. aqueous alkalis. Fe_2Cl_6 gives a red colouration. Conc. H_2SO_4 gives no colour on warming.

Reactions.—1. *Boiling water* splits it up into di-phenyl-methylene di-ketone, $(C_6H_5.CO)_2CH_2$, and CO_2.—2. Boiling dilute H_2SO_4 gives acetophenone, benzoic acid, and CO_2.

Salt.—AgA'.

Ethyl ether EtA'. Oil; not solid at −10°.

Methyl-benzoyl-acetic acid is (α)-BENZOYL-PROPIONIC ACID (*q. v.*).

Ethyl-benzoyl-acetic acid $BzCHEt.CO_2H$. [111°-115°]. From NaOEt and EtI on alcoholic $BzCH_2CO_2Et$, and saponifying the oily product by allowing it to stand for some days with alcoholic KOH (Baeyer a. Perkin, jun., *B.* 16, 2130; *C. J.* 45, 180; 47, 240). Small needles, melts about 115° with slight decomposition. Easily soluble in alcohol, ether, and benzene. Boiled with dilute alcoholic KOH, it gives phenyl-propyl-ketone; benzoic and butyric acids are also formed, especially if the potash be strong.

Ethyl ether EtA'. (232°) at 225 mm.

Propyl-benzoyl-acetic ether $BzCHPr.CO_2Et$. (239°) at 225 mm. Prepared like the preceding. Alkalis form phenyl-butyl-ketone. PCl_5 forms β-chloro-α-propyl-cinnamic ether.

Isopropyl-benzoyl-acetic ether $BzCHPr.CO_2Et$. (237°) at 225 mm. From benzoyl-acetic ether, Na, and PrI.

Iso-butyl-benzoyl-acetic ether $Bz.CH(CH_2.CHMe_2).CO_2Et$. (247°) at 225 mm. Prepared like the preceding (Perkin a. Calman, *C. J.* 49, 165).

Di-ethyl-benzoyl-acetic acid $BzCEt_2CO_2H$. [128°-130°]. From $Bz.CHEt.CO_2Et$ by NaOEt and EtI. The diethyl-benzoyl-acetic ether is saponified by standing for weeks with dilute alcoholic KOH (Baeyer a. Perkin, jun., *B.* 16, 2131; *C. J.* 45, 183). Heated alone or with dilute H_2SO_4 it gives off CO_2. Boiling dilute alcoholic KOH forms benzoic acid, diethylacetic acid, and di-ethyl-acetophenone (*v.* amyl-phenyl-ketone).

Tri-benzoyl-acetic ether. $CBz_3.CO_2Et$. From ethyl di-benzoyl-acetate, NaOEt, and BzCl (Perkin, jun., *C. J.* 47, 240). Thick yellow oil; sol. alcoholic KOH but reppd. by water. Boiling dilute H_2SO_4 forms acetophenone.

BENZOYL-ACETIC-ALDEHYDE $C_6H_5.CO.CH_2.CHO$. Prepared by dissolving sodium (1 atom) in 20 or 30 times its weight of absolute alcohol, cooling to 0°, and adding acetophenone (1 mol.) and formic ether (1 mol.). On long standing the sodium compound separates as a granular pp.; this is dissolved in water and the aldehyde ppd. by acetic acid. Colourless unstable oil. Cupric acetate gives a pp. of bright green needles, which soon change to dark-green prisms. It reacts with amines very readily.

Anilide $C_6H_5.CO.CH_2.CH:NC_6H_5$: [141°]; yellow prisms or plates; sol. hot alcohol.

p-Toluide $C_6H_5.CO.CH_2.CH:NC_7H_7$: [160°-163°]; small yellow crystals.

(β)-*Naphthylamide* $C_6H_5.CO.CH_2.CH:NC_{10}H_7$: [182°]; small bronzy crystals; sl. sol. almost all solvents (Claisen a. Fischer, *B.* 20, 2191).

BENZOYL-ACETIMIDO-ETHYLIC ETHER $C_6H_5.CO.CH_2.C(NH).OEt$. [89°·5 corr.].

Benzoyl-acetonitrile $C_6H_5.CO.CH_2.CN$ treated with alcoholic hydrochloric acid gives rise to $C_6H_5.CO.CH_2.C(NHHCl)OEt$ and this loses HCl when treated with ammonia giving the imido-ether (Haller, *Bl.* [2] 48, 24; *C. R.* 104, 1448).

Properties.—Prisms or tables. V. sol. ether.

Reactions.—KNO_2 and H_2SO_4 give the nitroso-derivative $C_6H_5.CO.CH_2.C(N.NO).OEt$ [117°], which gives Liebermann's reaction. The hydrochloride of the base dissolved in aqueous alcohol deposits MH_4Cl and benzoyl-acetic ether is left in solution.

Hydrochloride B'.HCl. [140° corr.]. Entangled needles. Insol. aq and ether. Strongly irritates the mucous membranes.

BENZOYL-ACETO-ACETIC ETHER *v.* p. 21.

BENZOYL-ACETO-CARBOXYLIC ACID *v.* ACETOPHENONE CARBOXYLIC ACID.

BENZOYL-ACETONE $C_{10}H_{10}O_2$ *i.e.* $C_6H_5.CO.CH_2.CO.CH_3$. *Phenyl methyl methylene di-ketone. Acetyl-acetophenone. Acetyl-benzoyl-methane.* [61°]. (261°).

Formation.—By the action of dry NaOEt upon a mixture of acetone and benzoic ether (Claisen, *B.* 20, 655).

Preparation.—1. Benzoyl-aceto-acetic ether, formed by the action of benzoyl chloride upon sodio-aceto-acetic ether, is boiled with water for a few hours; the yield is 25 p.c.—2. Prepared by adding acetophenone (1 mol.) to a cooled mixture of acetic ether (about 2 mols.) and alcohol-free sodium ethylate; yield: 80-90 p.c. of the acetophenone (Beyer a. Claisen, *B.* 20, 2078).

Copper compound $(C_{10}H_9O_2)_2Cu$: formed as a pale green pp. by adding cupric acetate to the alcoholic solution. It is m. sol. alcohol and benzene, from which it crystallises in bright green needles.

Amide $C_6H_5.CO.CH_2.C(NH).CH_3$: [143°]; clear glistening trimetric crystals, $a:b:c$ = ·9927:1:·8820.

Anilide $C_6H_5.CO.CH_2.C(NPh).CH_3$: [110°]; plates. By warming with H_2SO_4 (10 pts.) it is converted into (*Py.* 1:3)-phenyl-methyl-quinoline (Beyer, *B.* 20, 1770).

Properties.—Crystals; distils undecomposed; volatile with steam. Sol. hot water, alcohol, and ether. Dissolves in alkalis with a yellow colour. Sl. sol. strong acids. Fe_2Cl_6 gives a dark-red colouration.

Reactions.—By warming with alkalis or by long boiling with acids it yields acetophenone. It has slightly acid characters, the H of the central CH_2 group being replaceable as in aceto-acetic ether, since it lies between two CO groups. By heating with strong aqueous NH_3 at 120° it is converted into the imide $C_6H_5.C(NH).CH_2.CO.CH_3$ or $C_6H_5.CO.CH_2.C(NH).CH_3$. It condenses with (1 mol.) of phenyl-hydrazine with elimination of $2H_2O$, forming methyl-di-phenyl-pyrazol (Fischer a. Bülow, *B.* 18, 2131).

Salts.—$C_{10}H_9O_2Na$: small yellowish plates.—$C_{10}H_9O_2Ag$: white pp.; v. sl. sol. water (Fischer a. Kuzel, *B.* 16, 2239).

Oxim $C_{10}H_{11}O_2N$ *i.e.* $C_6H_5.C(NOH)CH_2.CO.CH_3$ or $C_6H_5.CO.CH_2.C(NOH).CH_3$. [66°]. Formed by heating benzoyl-acetone with hydroxylamine hydrochloride in alcoholic solution (Ceresole, *B.* 17, 812). White glistening scales. Volatile with steam. V. sol. acetone, benzene, and CS_2, insol. water.

Di-benzoyl-acetone $(C_6H_5.CO)_2:CH.CO.CH_3$. [102°]. Formed by the action of benzoyl chloride upon sodio-benzoyl acetone (Fischer a. Bülow, *B.* 18, 2133). Small needles. Sol. alcohol and ether, v. sl. sol. water. Sodium has no action upon it.

BENZOYL - ACETONIMIDE $C_{10}H_{11}NO$ *i.e.* $C_6H_5.C(NH).CH_2.CO.CH_3$ or $C_6H_5.CO.CH_2.C(NH).CH_3$. [143°]. Obtained by heating benzoyl acetone with strong aqueous NH_3 at 120° (Fischer a. Bülow, *B.* 18, 2134). Distils undecomposed. Small plates, or large quadratic crystals. V. sol. dilute acids, by heating with which it is converted back into benzoyl-acetone and NH_3.

BENZOYL-ACETONITRILE C_9H_7NO *i.e.* $C_6H_5.CO.CH_2.CN$.

Cyano-acetophenone. [81° cor.]. Formed by the action of boiling water on benzoyl-cyanacetic ether $C_6H_5.CO.CH(CN).CO_2Et$ (Haller, *Bl.* [2] 48, 23). White needles, sol. boiling water, alcohol, ether, and alkalis. Boiling conc. KOH acts thus: $C_6H_5.CO.CH_2.CN + 2KHO + H_2O = NH_3 + C_6H_5.CO_2K + CH_3.CO_2K$. In alcoholic solution gaseous HCl gives a body $C_{11}H_{14}O_2NCl$ (probably $C_6H_5.CO.CH_2.C(NHHCl)OEt$ [140corr.]; whence ammonia in the cold gives the imido-ether $C_6H_5.CO.CH_2.C(NH).OEt$). If the action of the alcoholic HCl is prolonged, the products are the same as with KOH.

Silver salt $C_6H_5.CO.CHAg.CN$. White pp. Insol. aq and alcohol; sol. ammonia.

BENZOYLACETOPHENONE *v.* DI-PHENYL METHYLENE DI-KETONE.

BENZOYL - ACETYL-ETHANE *v.* ACETO-PHENONE-ACETONE, p. 36.

Di-benzoyl-di-acetyl-ethane

$$C_{20}H_{18}O_4 \quad i.e. \quad \begin{array}{l} C_6H_5.CO.CH.CO.CH_3 \\ \quad\quad\quad\; | \\ C_6H_5.CO.CH.CO.CH_3 \end{array}.$$

Di phenyl-di-methyl-acetylene-tetra-ketone [175°]. Formed by the action of an ethereal solution of iodine upon 2 mols. of sodio-benzoyl-acetone (Fischer a. Bülow, *B.* 18, 2133). White needles. Sol. hot alcohol, sl. sol. ether, insol. water and dilute alkalis. Decomposed by boiling with alkalis.

BENZOYL-ACRYLIC ACID $C_6H_5.CO.CH:CH.CO_2H$. White plates, [64°], from water; after fusion its melting-point is altered to [97°]. Long needles, [99°] from toluene. Sl. sol. cold water and ligroin, v. sol. other solvents. Prepared by the action of Al_2Cl_6 on a mixture of benzene and maleic anhydride. By alkalis it is decomposed into acetophenone and glyoxylic acid. On heating by itself or with Ac_2O, it gives a red condensation product (Pechmann, *B.* 15, 885).

Bromine addition product [135°]. Colourless crystals.

BENZOYL-ALLOPHANIC ACID *v.* p. 127.

BENZOYL-ALLYL-ACETIC ACID *v.* ALLYL-BENZOYL-ACETIC ACID, p. 135.

BENZOYL-AMIDO- *v.* AMIDO-.

BENZOYL-AMIDO-ACETIC ACID *v.* HIPPURIC ACID.

BENZOYL - AMMELINE $C_{10}H_9N_5O_2$ *i.e.* $C_3H_4BzN_5O$. From sodium cyanamide and BzCl (Gerlich, *J. pr.* [2] 13, 272). Brown resin, insol. water and ether, sol. alcohol and aqueous alkalis. Resolved by distilling in a current of hydrogen into benzonitrile, carbonic oxide, and cyanamide.

BENZOYL-ANILIDE *v.* ANILINE.

BENZOYL - ANILINE *v.* AMIDO - BENZOPHENONE.

BENZOYL-ANISIDINE *v.* *Benzoyl-methyl-* AMIDO-PHENOL.

BENZOYL-AZOTIDE *v.* p. 478.

BENZOYL-BENZENE *v.* BENZOPHENONE.

Di-benzoyl-benzene *v.* PHTHALOPHENONE.

BENZOYL-BENZIDINE *v.* *Di-*AMIDO - DI-PHENYL.

BENZOYL-BENZOIC-ACETIC ANHYDRIDE $C_6H_5.CO.C_6H_4.CO.O.CO.CH_3$. [112°]. Prepared by heating *o*-benzoyl-benzoic acid with acetic anhydride to 100° (Freiher a. Pechmann, *B.* 14, 1865). Large crystals. Insol. alkalis. At 200° it decomposes into acetic and benzoyl-benzoic anhydrides.

o-BENZOYL-BENZOIC ACID $C_{14}H_{10}O_3$ *i.e.* $C_6H_5.CO.C_6H_4.CO_2H$ [1:2]. *Benzophenone carboxylic acid.* Mol. w. 226. [87°] (Z.); [94°] (Hemilian, *B.* 11, 838).

Formation.—1. By oxidation of *o*-benzyl-toluene (Zincke a. Plaskuda, *B.* 6, 907), phenyl-o-tolyl-ketone (Behr a. Van Dorp, *B.* 7, 17), or di-benzyl-benzene (Zincke, *B.* 9, 32) with chromic mixture.

Preparation.—150 grms. of Al_2Cl_6 are slowly added during 3 hours to a solution of 100 grms. of phthalic anhydride in 1000 grms. of benzene (pure), the benzene is then poured off and can be used at once for a fresh operation, whilst the solid residue is washed with dilute HCl and with water, dissolved in Na_2CO_3 and the acid precipitated from the solution by HCl, and finally recrystallised from xylene (3 pts.); the yield is 60 p.c. of the phthalic anhydride used (Friedel a. Crafts, *C. R.* 86, 1368; 92, 833; Freiherr a. Pechmann, *B.* 13, 1612).

Properties.—Triclinic needles (containing aq). When dry it melts at 128°.

Reactions.—1. P_2O_5 at 190° forms anthraquinone.—2. *Hot fuming sulphuric acid* forms anthraquinone sulphonic acid (Liebermann, *B.* 7, 805).—3. *Sodium amalgam* first reduces it to $C_6H_5.CH(OH).C_6H_4.CO_2H$ and then to $C_6H_5.CH_2.C_6H_4.CO_2H$.—4. *Resorcin, pyrogallol* &c., on heating, form phthaleins.—5. With phenyl-hydrazine it gives a condensation-product $C_6H_4\left\langle\begin{matrix} C\text{--}Ph \\ CO \end{matrix}\right\rangle N_2Ph$ [182°] (Roser, *B.* 18, 805). This forms small needles, sl. sol. alcohol, insol. water.

Salts. — CaA'_2. — BaA'_2. — ZnA'_2 2aq. — CuA'_2 aq.

Methyl ether MeA'. [52°]: prisms.

Ethyl ether EtA'. [58°].

Anhydride $(Bz.C_6H_4.CO)_2O$. [120°] (Pechmann, *B.* 14, 1866).

m-Benzoyl-benzoic acid $Ph.CO.C_6H_4.CO_2H$. [1:3]. [161°].

Formation.—1. From phenyl-*m*-tolyl-methane (10 g.), $K_2Cr_2O_7$ (60 g.), H_2SO_4 (90 g.) and water (270 g.) by boiling for 3 days (Rotering; Senff, *A.* 220, 237). It is purified by reduction to $Ph.CH(OH).C_6H_4.CO_2Na$ by sodium-amalgam, crystallising this salt from water and oxidising again with H_2SO_4 and $K_2Cr_2O_7$.—2. A quantitative yield is obtained by treating phenyl-*m*-tolyl-methane at 130° with bromine-vapour sufficient to form $Ph.CH_2.C_6H_4.CH_2Br$ and treating the product with chromic mixture for 12 hours.—3. From Bz_2O (1 mol.) and BzCl (2 mols.) in presence of $ZnCl_2$ (Doebner, *A.* 210, 277; *B.* 14, 648).—4. Formed as a by-product in the pre-

paration of isophthalophenone by the action of Al_2Cl_6 on a mixture of benzene and iso-phthalyl chloride (Ador, B. 18, 321).

Properties.—Long silky needles (from water or glacial acetic acid), or small plates (from alcohol). Sl. sol. cold water, v. sol. benzene or toluene, v. e. sol. alcohol or ether. May be sublimed as plates. Dissolves in conc. H_2SO_4 giving no colour. Potash-fusion gives benzoic acid. Reduced by sodium-amalgam to *exo*-oxy-benzyl-benzoic acid (*q. v.*).

Salts.—BaA'_2 3aq: white crystalline powder. BaA'_2 4aq: small plates.—CaA'_2 2aq: white crystalline powder.—AgA': white leaflets.

Methyl ether MeA' [62°].

p-Benzoyl-benzoic acid $C_6H_5.CO.C_6H_4.CO_2H$ [1:4]. [194°]. Formed by oxidation of phenyl-*p*-tolyl-methane, phenyl-*p*-tolyl-ketone, *p*-phenyl-benzophenone or di-benzyl-benzene (Zincke, *A.* 161, 98; *B.* 6, 907; 9, 32; Goldschmiedt, *M.* 2, 438). Monoclinic plates (from water). V. sl. sol. cold water; sl. sol. hot water (difference from the *o*- acid), v. sol. alcohol and ether, sl. sol. benzene. Sublimes in plates.

Salts. CaA'_2 2aq: needles.—BaA'_2 2aq. AgA': v. sl. sol. water.

Methyl ether MeA'. [107°]. Satiny plates.

Ethyl ether EtA'. [52°]. Monoclinic.

DI-BENZOYL-BENZOIC ACID $C_{21}H_{14}O_4$ *i.e.* $(C_6H_5.CO)_2.C_6H_3.CO_2H$. Two acids of this composition are formed, together with an acid $C_{15}H_{10}O_5$, by oxidising the hydrocarbon $C_{21}H_{20}$ obtained as a by-product in the preparation of benzyl-toluene (Weber a. Zincke, *B.* 7, 1153).

(α)-Acid. [82°]. Resinous, and forms resinous salts. Potash fusion forms benzoic acid and a small quantity of an acid $C_{14}H_{10}O_4$.

(β)-Acid. [212°]. Needles, insol. water, v. sol. alcohol and ether. Its salts are sl. sol. water. *Ethyl ether* EtA'. [107°].

DI-BENZOYL-BENZYLIDENE-DI-ACETIC ACID *v. Benzylidene-di* BENZOYL-DI-ACETIC ACID.

BENZOYL-BENZOTRICHLORIDE *v.* PHENYL TRI-CHLORO-TOLYL KETONE.

BENZOYL-BENZYL-ANILINE *v.* BENZYL-ANILINE.

BENZOYL-BENZYL CHLORIDE *v.* PHENYL CHLORO-TOLYL KETONE.

BENZOYL-BENZYLIDENE CHLORIDE *v.* PHENYL DI-CHLORO-TOLYL KETONE.

BENZOYL-BROMANILINE *v.* BROMO-ANILINE.

BENZOYL BROMIDE $C_6H_5.CO.Br.$ (219° i.V.). [a little below 0°]. S.G. [15] 1·57. Colourless fluid, which fumes in the air.

Preparation.—Benzoic acid (500 pts.) is warmed with phosphorus tribromide (740 pts.) and the product is separated from the phosphorous acid by distillation in *vacuo*; the yield is 400 pts. (Claisen, *B.* 14, 2473). The so-called benzoyl bromide of Liebig and Wöhler (*A.* 3, 266) and of Paternò was probably benzylidene-bromide-benzoate, $C_6H_5CHBr(OBz)$, a compound of benzoic aldehyde with benzoyl bromide.

BENZOYL-BROMO-NITRANILIDE *v.* BROMO-NITRO-ANILINE.

BENZOYL-BROMO-PHENOL *v.* BROMO-PHENOL.

DI-BENZOYL-ISOBUTYRIC ACID $(C_6H_5.CO.CH_2)_2CH.CO_2H$. *Di-phenacyl-acetic acid.* [133°]. Formed by loss of CO_2, by heating di-β-benzoyl-di-methyl-malonic acid $(Bz.CH_2)_2C(CO_2H)_2$. Silky needles. V. sol. alcohol, ether, acetic acid, and hot benzene, insol. ligroïn. — A'Na: glistening needles (Kues a. Paal, *B.* 19, 3147).

BENZOYL-CARBAMIC ACID. $C_8H_7NO_3$.

Ethyl ether $C_6H_5.CO.NH.CO_2Et$. [110°]. Formed by boiling benzoyl-thiocarbamic ether in alcoholic solution with PbO (Lössner, *J. pr.* [2] 10, 254). Needles (from dilute alcohol), sl. sol. water. Decomposed by aqueous KOH into KOBz, alcohol, NH_3, and K_2CO_3. Alcoholic KOH gives a pp. of $C_6H_5.CO.NK.CO_2Et$, v. e. sol. water.

BENZOYL-CARBINOL $Ph.CO.CH_2OH$ [86°]. $Ph.C(OH)_2.CH_2OH$ [74°]. *Exo-oxy-phenyl-methyl ketone. Oxy-acetophenone. Aceto-phenone alcohol. Phenacyl alcohol.*

Formation.—1. By the action of alkalis on the acetate or chloride, $C_6H_5.CO.CH_2Cl$.—2. From phenyl-glycol (2 g.) and HNO_3 (6 c.c. of S.G. 1·36). The mixture is warmed and, as soon as reaction sets in, it is cooled. The product is diluted, neutralised with Na_2CO_3, and the crystalline carbinol filtered off. Ether extracts a further quantity from the filtrate (Hunaeus a. Zincke, *B.* 10, 1487).

Properties. Prisms or plates (from benzoline). Large crystals (from alcohol or ether). V. sol. ether, alcohol, or $CHCl_3$. Large plates containing H_2O (from water or dilute alcohol). In drying these, decomposition readily occurs, benzoic aldehyde being formed. The carbinol combines with $NaHSO_3$. Readily reduces ammoniacal silver nitrate or Fehling's solution, the chief product of the oxidation being mandelic acid $C_6H_5.CH(OH).CO_2H$ (Breuer a. Zincke, *B.* 13, 635).

Reactions.—1. Heated alone it gives off benzoic aldehyde and a pungent body.—2. Heated with aqueous NaOH or *baryta* it becomes yellow and forms benzoic aldehyde.—3. Water at 140° acts similarly. — 4. With HCN it yields the nitrile of atroglyceric acid $CH_2(OH).CPh(OH).CO_2H$ (Plöchl a. Blümlein, *B.* 16, 1290).

Acetate $Ph.CO.CH_2OAc$. [49°]. (270°). From chloro-acetophenone and AgOAc (Graebe, *B.* 4, 34); or from the carbinol and Ac_2O (Zincke). Trimetric tables (from benzoline). V. sol. alcohol, ether, or chloroform. M. sol. benzoline.

Benzoate $Ph.CO.CH_2OBz$. [117°] (Zincke). From chloro aceto-phenone and AgOBz or from benzoyl-carbinol and Bz_2O. Small tables (from dilute alcohol). V. sol. ether, benzene, or $CHCl_3$.

BENZOYL-CHLORANILIDE *v.* CHLORO-ANILINE.

BENZOYL CHLORIDE $C_6H_5.CO.Cl$. [−1°] (Lieben, *A.* 178, 43). (198°). (194°) (Brühl, *A.* 235, 11). S.G. [15] 1·21; $^{20}_{4}$ 1·2122 (B.). V.D. 4·99 (calc. 4·90). $\mu_D = 1·5537$. S.V. 126·3 (Ramsay).

Formation.—1. From chlorine and benzoic aldehyde (Liebig a. Wöhler, *A.* 3, 262).—2. From benzoic acid and PCl_5 (Cahours, *A. Ch.* [3] 23, 334).—3. From benzoates and $POCl_3$ (Gerhardt, *A. Ch.* [3] 37, 291).—4. In small quantities, by the action of Cl upon mandelic acid or on benzoic ethers (Malaguti, *A. Ch.* [2] 70, 374).—5.

B. 19, 3232).—10. **In considerable quantity by heating benzaldehyde with glycocoll (Curtius a. Lederer, *B.* 19, 2462).**—11. Together with di- and tri-benzyl-amine, as a by-product, in the preparation of di-benzyl-hydroxylamine from hydroxylamine hydrochloride, benzyl chloride and NaOH (Walder, *B.* 19, 3293).

Properties.—Liquid, miscible with water, alcohol, and ether. Separated from water by KOH. Strongly alkaline, absorbs CO_2, forming a crystalline carbonate, and fumes with HCl. With cyanogen it forms a compound $(C_7H_9N)_2(CN)_2$ [140°] which crystallises from alcohol, and forms a hydrochloride $(C_7H_9N)_2(CN)_2 2HCl$ (Strakosch, *B.* 5, 693).

Salts.—B'HCl: large leaflets or flat tables. —B'HBr.—$B'_2H_2PtCl_6$: orange tables or yellow plates, sl. sol. water. - $B'_2H_2SO_4$.

Acetyl derivative $C_6H_5.CH_2.NHAc$ [61°]: (300°); crystalline solid, sol. water (Amsel a. Hofmann, *B.* 19, 1285; Strakosch, *B.* 5, 697; Rudolph, *B.* 12, 1297).

Di-benzylamine $C_{14}H_{15}N$ *i.e.* $NH(CH_2.C_6H_5)_2$. S.G. $\frac{14}{}$ 1·033.

Formation.—1. By the action of NH_3 on $C_6H_5CH_2Cl$ or by reduction of benzonitrile (*v. supra*). 2. By the action of bromine-water on tribenzylamine (Limpricht, *A.* 144, 313).- 3. By boiling benzoic aldehyde with ammonium formate (Leuckart a. Bach, *B.* 19, 2128). - 4. Occurs together with mono- and tri-benzylamine as a by-product in the preparation of di-benzyl-hydroxylamine from hydroxylamine hydrochloride, benzyl chloride, and NaOH. - 5. Formed by the action of PCl_3 upon di-benzyl-hydroxylamine and treatment with water, the reaction probably being:

$(C_7H_7)_2N.OH + PCl_3 = (C_7H_7)_2N.O.PCl_2 + HCl$ and $(C_7H_7)_2N.O.PCl_2 + 3H_2O =$
$(C_7H_7)_2NH + H_3PO_4 + 2HCl$ (Walder, *B.* 19, 3287).

Properties. - Liquid, insol. water, v. sol. alcohol and ether. Does not absorb CO_2 from the air. On distillation it decomposes into s-di-phenyl-ethane, s-di-phenyl-ethylene, lophine, and various bases (Brunner, *A.* 151, 133).

Salts.—$B'HNO_3$: [186°], very sparingly soluble thin glistening needles.—B'HCl [256°]. —B'HBr [276°]. - B'HI [224°].— $B'_2H_2PtCl_6$: golden-yellow needles.

Nitrosamine $(C_6H_5.CH_2)_2N.NO$: [61°]; white crystals: v. sol. alcohol and ether, insol. water (W., *cf.* Rohde, *A.* 151, 366).

Picryl derivative $(C_6H_5.CH_2)_2N.OC_6H_2(NO_2)_3$ [171°]; orange plates.

Formyl derivative $(C_6H_5.CH_2)_2N.CHO$: [52°]; (above 360°) (Leuckart a. Bach, *B.* 19, 2128).

Di-sulphonic acid $C_{14}H_{13}N(SO_3H)_2$ (Limpricht, *A.* 144, 317).—BaA".

Tri-benzylamine $C_{21}H_{21}N$ *i.e.* $(C_6H_5.CH_2)_3N$. [91°].

Formation.—1. From benzyl chloride and NH_3 (*v. supra*).—2. By heating di-benzylamine with benzyl chloride at 100° (Walder, *B.* 19, 3287).—3. Together with mono- and di-benzylamine as a by-product in the preparation of di-benzyl-hydroxylamine from hydroxylamine hydrochloride, benzyl chloride, and NaOH (W.). 4. **By heating benzaldehyde with rather more than an equal weight of ammonium formate; the yield is 40 p.c. of the benzaldehyde employed (Leuckart, *B.* 18, 2341). White plates (from hot alcohol); v. sl. sol. water. When heated for a long time with MeI or EtI at 150°,** benzyl iodide and tetra-methyl- (or ethyl-) ammonium iodide are formed (Marquardt, *B.* 19, 1027). Fuming sulphuric acid forms $C_{21}H_{18}(SO_3H)_3N$ (Limpricht, *A.* 144, 311).

Salts.—B'HCl: [228°]; thick prisms or iridescent plates, v. sol. hot alcohol, insol. water. - $B'_2H_2Cl_2PtCl_4$: orange yellow needles.— $B'HNO_3$: [125°]; insol. water. B'HBr: [208°]. —$B'HBr_3$.- B'HI: [178°].- $B'HAl(SO_4)_2$ 12aq: [110°]; sol. water.

Methylo-iodide B'MeI: [184°]; needles or plates; sol. hot alcohol, sl. sol. cold water.

Methylo-hydrate B'Me(OH): crystalline solid; alkaline reaction; v. sol. water. On heating it evolves MeOH forming tri-benzylamine.

Methylo-chloride-platinum-salt $(B'MeCl)_2PtCl_4$: [197°]; orange pp.; insol. cold water and alcohol.

Ethylo-iodide B'EtI: [190°]; colourless rhombic crystals; sol. alcohol and hot water.

Isopropylo-iodide B'PrI: [170°]; needles; sl. sol. hot water.

BENZYLAMINE-ω-DI-SULPHONIC ACID $C_6H_5.CH(SO_3H).NH(SO_3H)$. The di sodium salt $A''Na_2$ 3aq is formed by shaking benzaldoxim with a 30 p.c. sodium bisulphite solution. It crystallises in small white needles, v. e. sol. water, insol. cold alcohol. By warming with dilute acids it is split up into benzaldehyde, sodium sulphate, and ammonium sulphite:

$C_6H_5.CH(SO_3Na).NH(SO_3Na) + 2H_2O$
$= C_6H_5.CHO + Na_2SO_4 + (NH_4)HSO_3$.

Alkalis decompose it in the cold, and water on boiling (Pechmann, *B.* 20, 2539).

BENZYL-ANILINE $C_6H_5.NH(C_7H_7)$. [33° uncor.]. (above 360°). Obtained by reducing thio-benzoyl-aniline (Bernthsen a. Trompeter, *B.* 11, 1760). Formed also by boiling diazobenzene-benzyl-anilide (50 g.) with HCl (200 c.c.); the yield is 20 g. (Friswell a. Green, *B.* 19, 2036). Yellowish crystals.

Salts.—B'HCl [203° uncor.]; white plates; decomposed by water.- $B'_2H_2Cl_2PtCl_4$ [168° uncor.]; slender yellow needles; tolerably easily soluble in water.- $B'_2C_2H_2O_4$.—$B'CdCl_2$.

Benzoyl derivative [104°] (Fleischer, *A.* 138, 229).

Di-benzyl-aniline $C_6H_5.N(CH_2.C_6H_5)_2$. [67°]. (above 300°). Prepared by heating a mixture of aniline (54 pts.), benzyl chloride (150 pts.) and NaOH (30 pts.) on the water-bath for three or four weeks. After cooling the solidified cake is pressed, distilled with steam to remove excess of benzyl chloride, washed with hot water, and crystallised from alcohol. Colourless needles. V. sol. ether, benzene, hot alcohol and hot acetic acid, sl. sol. cold alcohol and cold acetic acid, nearly insol. water. Weak base.

Salts. — B'HClaq: glistening prisms. — $B'_2H_2Cl_2PtCl_4$: thin orange - yellow scales. Picrate $B'C_6H_2(NO_2)_3OH$: [132], long yellow needles (Matzudaira, *B.* 20, 1611).

TRI-BENZYL-ARSINE *v.* p. 322.

BENZYL-BARBITURIC ACID *v.* BARBITURIC ACID.

BENZYL-BENZENE *v.* DI-PHENYL-METHANE.

p-**Di-benzyl-benzene** $C_{20}H_{18}$ *i.e.* $(C_6H_5.CH_2)_2C_6H_4$. [86°]. Formed, together with

the *o*-isomeride and di-phenyl methane, by the action of zinc on a mixture of benzyl chloride and benzene, or by the action of H_2SO_4 on a mixture of benzene and methylal, $CH_2(OMe)_2$ (Zincke, *B.* 6, 119, 221; 9, 31). Transparent laminæ, sl. sol. ether, v. sol. benzene and hot alcohol. CrO_3 forms (a)-dibenzoyl-benzene and *p*-benzoyl-benzoic acid.

o-**Di-benzyl-benzene** $(C_6H_5.CH_2)_2C_6H_4$. [78°]. Silky needles (from alcohol); v. sol. ether and alcohol. CrO_3 forms *o*-di-benzoyl-benzene and *o*-benzoyl-benzoic acid.

BENZYL BENZOATE $C_{14}H_{12}O_2$ *i.e.* $C_6H_5.CH_2.O.CO.C_6H_5$. (324° i.V.). [21°]. S.G. (fluid, at 19°) 1·1224. From benzyl alcohol and BzCl (Kraut, *A.* 152, 130). Formed also by several days' heating of benzaldehyde at 100° with a small quantity of sodium benzylate; probably the compound $C_6H_5.C(OC_7H_7)_2ONa$ is first formed and then decomposes into benzyl benzoate and sodium benzylate, which latter again reacts upon a further quantity of benzaldehyde, producing more of the intermediate product, and so on. Large colourless crystals (Claisen, *B.* 20, 646).

o-**BENZYL-BENZOIC ACID** $C_{14}H_{12}O_2$ *i.e.* $C_6H_5.CH_2.C_6H_4.CO_2H$. Mol. w. 212. [114°]. From *o*-benzoyl-benzoic acid and sodium-amalgam (Rotering, *J.* 1875, 598; *B.* 9, 633). Slender needles; may be sublimed; sl. sol. cold water, v. sol. alcohol and ether. $CaA'_2$2aq. – $CaA'_2$3½ aq. $BaA'_2$5½ aq. AgA'. MeA'.

m-**Benzyl-benzoic acid** $Ph.CH_2.C_6H_4.CO_2H$. [108°].

Formation.—1. From *exo*-oxy-benzyl-benzoic acid, $Ph.CH(OH).C_6H_4.CO_2H$ and conc. HI at 170°.—2. From *exo*-bromo-*m*-toluic acid, $CH_2Br.C_6H_4.CO_2H$, benzene and Al_2Cl_6 (Senff, *A.* 220, 247). Yield 50 p.c. of theoretical from toluic acid.—3. A small quantity from benzoic ether, benzyl chloride, and $ZnCl_2$ by boiling.

Properties.—Short slender needles (from hot water), small plates (from hot dilute alcohol); sl. sol. cold water, m. sol. hot water, v. e. sol. alcohol, ether or chloroform. Conc. H_2SO_4 forms a colourless solution. $K_2Cr_2O_7$ and H_2SO_4 give *m*-benzoyl-benzoic acid.—CaA'_2aq.—$BaA'_2$4aq.—AgA'.

p-**Benzyl-benzoic acid** $Ph.CH_2.C_6H_4.CO_2H$ [1:4]. [155°].

Formation.—1. By oxidising *p*-benzyl-toluene with dilute H_2SO_4 (Zincke, *A.* 161, 105).—2. By reducing *exo*-oxy-*p*-benzyl benzoic acid with HI. 3. From *p*-benzoyl-benzoic acid and sodium-amalgam or HI and P (Graebe, *B.* 8, 1054).

Properties.—Minute needles (from water); may be sublimed; sl. sol. cold water, v. sol. alcohol and ether. Chromic mixture oxidises it to *p*-benzoyl-benzoic acid.—CaA'_2HA'.—$BaA'_2$2aq. AgA'.

BENZYL BROMIDE $C_6H_5.CH_2Br$. (199°). S.G. $\frac{22}{0}$ 1·4380.

Formation.—1. From benzyl alcohol and HBr (Kekulé, *A.* 137, 190).—2. From Br and boiling toluene (Beilstein, *A.* 143, 369; Jackson a. Field, *Am.* 2, 11).—3. From benzyl chloride and $AsBr_3$ (Brix, *A.* 225, 163).

Preparation.—By the action of bromine (1 mol.) upon cold toluene (1 mol.) in direct sunshine; the yield is quantitative (Schramm, *B.* 18, 608).

Properties.—Pungent liquid. The zinc-copper couple acts vigorously upon it, producing two isomeric benzylenes. In presence of ether, the zinc-copper couple produces dibenzyl, $ZnBr_2$, and C_7H_7ZnBr, whence water produces toluene: $2C_7H_7ZnBr + 2H_2O = 2C_7H_8 + ZnBr_2 + Zn(OH)_2$. In presence of alcohol, the couple produces toluene and EtOZnBr. In presence of water, the couple produces dibenzyl and a little toluene (Gladstone a. Tribe, *C. J.* 47, 448).

BENZYL BUTYRATE $C_{11}H_{14}O_2$ *i.e.* $C_6H_5.CH_2.O.CO.Pr$. (240°). S.G. $\frac{16}{17.5}$ 1·016 (Conrad a. Hodgkinson, *A.* 193, 320).

Benzyl isobutyrate $Me_2CH.CO_2.CH_2Ph$. (228° i. V.). S.G. $\frac{22}{17}$ 1·016. Prepared by boiling an alcoholic solution of benzyl chloride and potassic isobutyrate for five days with inverted condenser. The product is mixed with water and the oil distilled.

Properties.—Oil, with pleasant odour.

Reactions.—When benzyl isobutyrate (90 g.) is heated with sodium (8 g.) a violent action occurs, the products being hydrogen, sodic isobutyrate, benzylic benzyl-isobutyrate (*q.v.*), sodic benzoate, toluene, and an oil $(C_{14}H_{18}O)_n$, (340°–350°). The principal reaction is:

$$4Me_2CH.CO_2.CH_2Ph + Na_2 =$$
$$2Me_2C(CH_2Ph).CO_2C_7H_7 + 2Me_2CH.CO_2Na + H_2$$

(W. R. Hodgkinson, *C. J.* 33, 496).

a-**BENZYL-ISOBUTYRIC ACID** $C_{11}H_{14}O_2$ *i.e.* $Me_2C(CH_2Ph)CO_2H$.

Benzyl ether $(C_7H_7)A'$. (280°–285°). S.G. $\frac{18}{17.5}$ 1·0285. Prepared by the action of sodium on benzyl-isobutyrate (*q. v.*).

Reactions.—1. Heated with *sodium* a violent action occurs, toluene, sodic benzoate, sodic benzyl-isobutyrate and an oil, $C_{14}H_{18}O$ (350°–355°) being formed.—2. It is attacked by *alkalis* with great difficulty, the saponification gives isobutyric not benzyl-isobutyric acid (W. R. Hodgkinson, *C. J.* 33, 503; *A.* 201, 171).

BENZYL CARBAMATE $NH_2.CO.O.C_7H_7$. [86°]. From benzyl alcohol and urea nitrate at 140° (Campisi a. Amato, *B.* 4, 412) or solid cyanogen chloride (Cannizzaro, *B.* 3, 518). Large plates (from water); sl. sol. hot water, v. sol. alcohol. Decomposes above 200° into benzyl alcohol and cyanuric acid.

BENZYL-CARBAMIC ACID $C_7H_7NH.CO.OH$.

Benzyl-ammonium salt $C_7H_7NH.CO_2NH_3C_7H_7$. [99°]. From benzylamine and CO_2. Formed also by heating *a*-amido-phenyl-acetic acid at 260°; the yield being nearly the theoretical (Tiemann a. Friedländer, *B.* 14, 1969). Plates, sol. water and alcohol, insol. ether; volatile with steam. Decomposed by acids or alkalis into CO_2 and benzylamine.

BENZYL DI-CARBOXY-GLUTACONIC ACID *v.* DI-CARBOXY-GLUTACONIC ACID.

DIBENZYL-CARBOXYLIC ACID *v.* DI-PHENYL-ETHANE-CARBOXYLIC ACID.

DIBENZYL DI-CARBOXYLIC ACID *v.* DI-PHENYL-SUCCINIC ACID and DI-PHENYL-ETHANE DI-CARBOXYLIC ACID.

BENZYL CARBINOL *v.* PHENYL-ETHYL ALCOHOL.

BENZYL CHLORIDE C_7H_7Cl *i.e.* $C_6H_5.CH_2Cl$. Mol. w. 126·5. *ω-Chloro-toluene.* (178°) at 754 mm. S.G. $\frac{178}{4}$ 0·9453. S.V. 133·45 (Schiff, *B.* 19, 563; *A.* 220, 98); 133·18 (Ramsay).

Formation.—1. From benzyl alcohol and HCl (Cannizzaro, *A.* 88, 129; 96, 246; Deville, *A. Ch.* [3] 3, 178).—2. By distilling toluene in a current of chlorine (Lauth a. Grimaux, *Bl.* 1867, i. 105).

Preparation.—By passing chlorine (1 mol.) into cold toluene (1 mol.) exposed to direct sunshine; the yield is nearly theoretical (Schramm, *B.* 18, 608).

Properties.—Oil, sol. alcohol and ether.

Reactions.—1. Boiling alcoholic KOH forms C_7H_7OEt.—2. Alcoholic KOAc forms C_7H_7OAc.—3. Alcoholic KCN forms C_7H_7CN.—4. Alcoholic NH_3 forms, on heating, mono-, di-, and tri-benzylamine.—5. Hot dilute HNO_3 (or a nitrate) forms benzoic aldehyde.—6. Boiling $Pb(OH)_2$ forms benzyl alcohol.—7. KOPh forms phenyl benzyl oxide.—8. *Water* at 180° gives a product which, on distillation, yields benzyl-toluene and anthracene. Before distillation the product is perhaps $C_6H_5.CH_2.C_6H_4.CH_2Cl$ (Van Dorp, *B.* 5, 1070; Zincke, *B.* 7, 276).—9. Long boiling with water (30 vols.) produces benzyl alcohol.—10. *Sodium-amalgam* produces a little *s*-di-phenyl-ethylene.—11. *Aromatic hydrocarbons* in presence of powdered zinc give off HCl and form condensation products (Zincke, *B.* 6, 137).—12. *Chloroformic ether* and *sodium* form di-phenyl-ethane exo-carboxylic ether, $PhCH_2.CHPh.CO_2Et$ (Wurtz, *C. R.* 70, 350).—13. Heated with Al_2Cl_6 it gives off HCl, forming toluene and anthracene (Perkin, jun. a. Hodgkinson, *C. J.* 37, 726).—14. In carbon disulphide solution yields, when chromyl chloride is added gradually, a brown precipitate of composition $PhCH_2Cl, CrO_2Cl_2$, slowly converted by moist air into benzoic aldehyde;

$$3Ph.CHCl.O.Cr(OH)Cl_2 + 3H_2O$$
$$= 9HCl + Cr_2O_3 + CrO_3 + 3PhCHO.$$

The compound heated to 170° loses HCl, forming a compound $PhCHClCrO_2Cl$, which also yields benzoic aldehyde.

$$3PhCHCl.O.CrO.Cl + 3H_2O$$
$$= 6HCl + Cr_2O_3 + CrO_3 + 3PhCHO$$ (Etard, *A. Ch.* [5] 22, 235).—15. HI reduces it to toluene.—16. *Zinc dust* gives toluene, phenyl-tolyl-methane, and anthracene (Frost, *Bl.* [2] 46, 249).

BENZYL-CHLORO-MALONIC ACID *v.* CHLORO-BENZYL-MALONIC ACID.

BENZYL-CINCHONINE *v.* CINCHONINE.

α-BENZYL-CINNAMIC ACID $C_{16}H_{14}O_2$ *i.e.* $C_6H_5.CH:C(CH_2Ph).CO_2H$. [157°]. Formed by the action of alkalis on the compound $Ph.SO_2.C(CH_2Ph)_2.CO_2Et$ (Michael a. Palmer, *Am.* 7, 70). Large white needles, insol. water, sol. alcohol.

***p*-BENZYL-CRESOL** $C_6H_5.CH_2.C_6H_3Me.OH$. (240°) at 40 mm. From benzyl chloride, cresol, and zinc (Mazzara, *G.* 8, 303; 11, 438; 12, 264).

Reactions.—1. *Chloro-acetic acid* and KOHAq form $C_6H_5.CH_2.C_6H_3Me.O.CH_2.CO_2H$ [111°].—2. (α)-*chloropropionic acid* forms $C_6H_5.CH_2.C_6H_3Me.OCHMe.CO_2H$ [115°].—3. CO_2 and Na forms $C_6H_5.CH_2.C_6H_2(OH).CO_2Na$.

Acetyl derivative $C_{14}H_{13}AcO$. (245°) at 40 mm.

BENZYL CRESYL OXIDE $C_6H_5.CH_2.O.C_6H_4.CH_3$, *v.* *Tolyl ether of* BENZYL ALCOHOL.

BENZYL CYANAMIDE $C_8H_8N_2$ *i.e.* $C_6H_5.CH_2.NH.CN$. [53°]. Formed by passing CyCl into benzylamine in ether (Strakosch, *B.* 5, 694). Plates (from ether); insol. water, v. e. sol. alcohol and ether. On keeping it changes to isomeric tri-benzyl-melamine. Boiling HCl forms benzyl-urea.

Di-benzyl-cyanamide $(C_6H_5CH_2)_2N.CN$. [54°]. From CyCl and dibenzylamine in alcohol (Limpricht, *A.* 144, 317). Plates; insol. water.

BENZYL CYANATE $C_6H_5.CH_2.N.CO$. (175°–200°). Formed, together with benzyl cyanurate, by the action of silver cyanate on benzyl chloride or bromide (Letts, *C. J.* 25, 446; Ladenburg a. Struve, *B.* 10, 46). Pungent liquid. Changes spontaneously into the cyanurate. Alcoholic NH_3 converts it into benzyl-urea.

BENZYL CYANIDE *v.* PHENYL-ACETONITRILE.

BENZYL CYANURATE $(C_6H_5CH_2)_3N_3C_3O_3$. [157°]. (above 320°). The chief product of the action of silver cyanate on benzyl chloride (*v. supra*); formed by isomeric change from benzyl cyanate. Silky needles (from alcohol), insol. water. Potash fusion gives K_2CO_3 and benzylamine.

BENZYL CYMENE $C_{17}H_{20}$ *i.e.* $C_6H_5.CH_2.C_6H_3MePr$. [297°] (Mazzara, *G.* 8, 508; [308°] (Weber, *J.* 1878, 402). S.G. 1° ·97. From benzyl chloride, cymene, and zinc. On oxidation it gives benzoyl-terephthalic acid.

Benzyl-cymene disulphonic acid $C_{17}H_{18}(SO_3H)_2$ (M.).

BENZYL-DURENE *v.* BENZYL-TETRA-METHYL-BENZENE.

BENZYLENE $(C_7H_6)_n$. Two hydrocarbons of this composition are formed by the action of the copper-zinc couple upon benzyl bromide (or chloride). (α)-benzylene, [42°]; μ_F ·6091, is a yellowish-red resin, sl. sol. alcohol, v. sol. ether and benzene. (β)-benzylene is a brown resin, insol. alcohol or ether (Gladstone a. Tribe, *C. J.* 47, 448).

BENZYLENE- *v.* BENZYLIDENE-.

BENZYLENE-DIAMINE *v.* AMIDO BENZYL-AMINE.

BENZYLENE-IMINE C_7H_7N *i.e.*

$C_6H_4\left\langle\begin{array}{l}CH_2\\ \;|\\ NH\end{array}\right.$ [1:2]. Formed by reduction of *o*-nitro-benzyl-chloride with $SnCl_2$ in conc. HCl. Greyish yellow powder. Sol. chloroform and acetic acid. Dissolves in HCl to a red fluorescent solution. The salts are amorphous. The *hydrochloride* forms a reddish-yellow transparent solid (B'HCl). The *platinochloride* $(B'_2H_2PtCl_6)$ is an insoluble, amorphous, reddish-brown powder (Lellmann a. Stickel, *B.* 19, 1611).

BENZYL ETHER $C_{14}H_{14}O$ *i.e.* $(C_6H_5.CH_2)_2O$. *Di-benzyl ether, Di-benzyl oxide.* (298° i. V.) S.G. [16] 1·036. μ 1·5525. Formed by heating benzyl alcohol with B_2O_3 at 120° (Cannizzaro, *A.* 92, 115). Also by heating benzyl chloride with water at 190° (Limpricht, *A.* 139, 313). From benzyl chloride and sodium benzylate (Lowe, *C. J.* 51, 700). Decomposed by heat into toluene and benzoic aldehyde.

BENZYL-DI-ETHYL-AMINE $C_{11}H_{17}N$ *i.e.* $C_6H_5.CH_2.NEt_2$. (212° cor.). From benzylamine and EtI at 130° (Ladenburg a. Struve, *B.* 10, 47, 561, 1152, 1634); or from di-ethyl-amine and

benzyl chloride at 100° (V. Meyer, *B.* 10, 310, 964).

Ethylo-iodide $C_6H_5.CH_2.NEt_3I$. Large crystals, v. sol. water. On dry-distillation it gives triethylamine and benzyl iodide.—$C_6H_5.CH_2.NEt_3I_2$[87°]—$(C_6H_5.CH_2.NEt_3Cl)_2PtCl_4$.

Di-benzyl-ethyl-amine $C_{16}H_{19}N$ *i.e.* $(C_6H_5.CH_2)_2NEt$. From di-benzyl-amine and EtI (Limpricht, *A.* 144, 315).—B'HCl.

Ethylo-iodide $(C_6H_5.CH_2)_2NEt_2I$. Sl. sol. cold water.

BENZYL-ETHYL-BENZENE $C_{15}H_{16}$ *i.e.* $C_6H_5.CH_2.C_6H_4.Et$ [1:4]. Mol. w. 196. (295° i.V.). S.G. $\frac{19}{}$ ·99. From benzyl chloride, ethyl-benzene, and zinc (Walker, *B.* 5, 686) or from *p*-ethyl-benzophenone, HI, and P (Söllscher, *B.* 15, 1682). Oxidation gives *p*-benzoyl-benzoic acid.

BENZYL ETHYL OXIDE *v.* BENZYL ALCOHOL.

BENZYL ETHYL KETONE $C_{10}H_{12}O$ *i.e.* $C_6H_5.CH_2.CO.C_2H_5$. Mol. w. 148. (c. 226°). S.G. $\frac{22}{}$ 1·00. From phenyl-acetic chloride and $ZnEt_2$ (Popoff, *B.* 5, 501). Does not combine with $NaHSO_3$. Oxidised by CrO_3 to benzoic and propionic acids.

BENZYL-*p*-ETHYLPHENYL-CARBINOL $C_6H_5.CH_2.CH(OH).C_6H_4.C_2H_5$ [1:4]. (350°). Liquid. Formed by heating benzyl ethylphenyl-ketone with alcoholic KOH at 160°. Boiled with dilute H_2SO_4 it gives phenyl-ethylphenyl-ethylene (Söllscher, *B.* 15, 1681).

BENZYL ETHYLPHENYL *p*-KETONE $C_6H_5.CH_2.CO.C_6H_4.C_2H_5$ [1:4]. *Ethyl-desoxybenzoïn.* [64°]. Prepared by the action of Al_2Cl_6 on a mixture of ethyl-benzene and phenyl-acetyl chloride (Söllscher, *B.* 15, 1680). Boils undecomposed. V.D. 8·03 (obs.). Small plates. Sol. ether, benzene, and hot alcohol, sl. sol. cold alcohol. On oxidation it gives terephthalic acid. On reduction it gives phenyl-ethylphenyl-ethane.

BENZYL-ETHYLPHENYL-METHANE *v.* PHENYL-ETHYLPHENYL-ETHANE.

BENZYL-DI-ETHYL SULPHINE. *Platino-chloride* $(C_6H_5CH_2.SEt_2Cl)_2PtCl_4$. From EtI and di-benzyl sulphide, the product being treated with AgCl and $PtCl_4$ successively (Schöller, *B.* 7, 1274).

DI-BENZYL-ETHYL *pseudo*-THIOUREA $C_{17}H_{20}N_2S$ *i.e.* $C_2H_5S.C(NH_2):NH$. Formed by heating di-benzyl-thiourea with ethyl iodide at 100°. Oil.

Salts. B'HI: [93°]; monoclinic prisms; v. sol. alcohol, sl. sol. water. $B'H_2SO_4$: large foursided rhombic soluble tables.—$B'_2H_2PtCl_6$: fine needles (Reimarus, *B.* 19, 2349).

BENZYL-FLUORENE $C_{20}H_{16}$ *i.e.* $C_6H_5.CH_2.C_6H_3<\begin{smallmatrix}CH_2\\C_6H_4\end{smallmatrix}>$. [102°]. Formed by heating fluorene with benzyl chloride and zinc-dust (Goldschmiedt, *M.* 2, 443). Plates (from alcohol).

BENZYL-FORM-ALDEHYDE *v.* PHENYL-ACETIC ALDEHYDE.

DI-BENZYL-GLYCOLLIC ACID $C_{16}H_{16}O_3$ *i.e.* $(C_6H_5CH_2)_2C(OH)CO_2H$. *Oxatoluic acid. a-Oxy-di-phenyl-iso-butyric acid.* [157°].

Formation.—1. From the nitrile and conc. HCl at 140°–160° (Spiegel, *A.* 219, 46; *B.* 13, 2219; 14, 1687).—2. By boiling vulpic acid (*q. v.*) with aqueous KOH: $C_{19}H_{14}O_5 + 3H_2O = CH_4O + 2CO_2 + C_{16}H_{16}O_3$ (Möller a. Strecker, *A.* 113, 56).

Rhombic prisms (from alcohol): $a:b:c = $ ·5113:1: ·3058. Fluffy mass of needles (from benzene). Salt.—AgA'.

Reactions.—1. HNO_3 gives a viscid nitro-acid (Möller a. Strecker).—2. Conc. aqueous KOH gives toluene and oxalic acid on boiling.—3. Treated with PCl_5 and H_2O successively a monophosphate, $C_{16}H_{15}O_3PO_3H_2$, crystallising in prisms, [160°] is formed.

Acetyl derivative. [106°]. Plates in rosettes (from $CHCl_3$ mixed with petroleum).

Methyl ether MeA': [71°]; needles.

Anhydride $C_{16}H_{14}O_2$. [169°]. Got by heating the acetyl derivative. Prisms (from benzene). V. sol. alcohol and ether. Na_2CO_3 Aq converts it into sodium di-benzyl-glycollate.

Nitrile $(C_6H_5CH_2)_2C(OH).CN$. [113°]. From di-benzyl ketone, KCN and HCl. Colourless flat rhombs (from alcohol). At 113° it splits up into HCN and di-benzyl ketone.

Amide. [193°]. From the nitrile and conc. HCl at 125°. Fluffy mass of long needles.

BENZYL-GLYOXALINE $C_3H_3(C_7H_7)N_2$. [71°]. (310°). Formed by the action of benzyl chloride on glyoxaline (Wallach, *B.* 16, 539). Colourless crystals. Sl. sol. ether, insol. cold water.—$B'_2H_2Cl_2PtCl_4$: yellow pp., insol. cold water.

DI-BENZYL-GUANIDINE $C_{15}H_{17}N_3$ *i.e.* $(C_6H_5.CH_2NH)_2C:NH$. [100°]. Formed by boiling benzylamine hydrochloride with benzyl-cyanamide in alcohol (Strakosch, *B.* 5, 695).—Laminæ (from alcohol). Sol. water, alcohol, and ether.—B'HCl [176°].

BENZYL-HYDROXYLAMINE *v.* HYDROXYLAMINE.

BENZYLIDENE. The radicle $C_6H_5.CH$, also called *benzal* or *benzylene*. The latter name is more appropriate to the isomeric radicle $C_6H_4.CH_2$.

BENZYLIDENE-DI-ACETAMIDE $C_{11}H_{14}N_2O_2$ *i.e.* $C_6H_5CH(NH.CO.CH_3)_2$. Formed by boiling acetamide with benzoic aldehyde (Roth, *A.* 154, 72; *Z.* [2] 4, 650; 6, 680). Silky crystals, sl. sol. cold water and ether. Not affected by boiling KOHAq but decomposed by hot HClAq into benzoic aldehyde and NH_4Ac.

BENZYLIDENE DI-ACETATE $C_{11}H_{12}O_4$ *i.e.* $CHPh(OAc)_2$. *Di-acetyl-benzoic ortho-aldehyde.* [45°]. From benzoic aldehyde and Ac_2O or from benzylidene chloride and AgOAc (Geuther, *A.* 106, 251; Wicke, *A.* 102, 368; Hübner, *Z.* 1867, 277; Neuhof, *A.* 146. 323; Limpricht, *A.* 139, 321; Perkin, *Z.* 1868, 172).

BENZYLIDENE-ACETIC ACID *v.* CINNAMIC ACID.

Benzylidene-di-acetic acid *v.* PHENYL-GLUTARIC ACID.

BENZYLIDENE-ACETO-ACETIC ACID *v.* p. 24.

BENZYLIDENE-DI-ACETO ACETIC-ETHER $C_{19}H_{24}O_6$ *i.e.* $C_6H_5.CH\{CH.CH(CO_2Et).CO.CH_3\}_2$(?). [153°]. Formed together with dehydro-benzylidene-di-acetoacetic ether $C_{19}H_{22}O_5$, by the action of benzoic aldehyde (1 mol.) upon aceto-acetic ether (2 mols.) in presence of a primary amine. Long white needles. Sl. sol. cold alcohol and ether (Hantzsch, *B.* 18, 2583).

Dehydro-benzylidene-di-acetoacetic-ether $C_{19}H_{22}O_5$ possibly

$$\begin{array}{c} \quad\quad Ph \\ EtCO_2-C-CH-C-CO_2Et. \\ \| \quad\quad\quad \| \\ MeC-O-CMe \end{array}$$

[88°]. Formed as described above. Glistening prisms. V. sol. cold or hot solvents (Hantzsch, *B.* 18, 2583).

BENZYLIDENE-DI-ACETONAMINE *v.* p. 27.

BENZYLIDENE-ACETONE $C_{10}H_{10}O$ *i.e.* Ph.CH:CH.CO.CH_3. *Aceto-cinnamone. Methyl-styryl ketone.* [42°] (152°) at 25 mm. (261° i.V.) at 760 mm.

Formation. — 1. From benzoic aldehyde, acetone and a little $ZnCl_2$ at 260° (Claisen a. Claparède, *B.* 14, 2461). · 2. By heating a mixture of calcium acetate with calcium cinnamate; also in small quantity by heating cinnamic aldehyde with Na and MeI at 130°, or by boiling cinnamic aldehyde with MeOH and $ZnCl_2$ (Engler a. Leist, *B.* 6. 254).

Preparation.—From benzoic aldehyde (20 g.), acetone (40 g.), water (1800 c.c.) and aqueous (10 p.c.) NaOH (20 g.) in the cold. After four days the oil that has separated is extracted with ether, dried over $CaCl_2$ and rectified *in vacuo* (Claisen a. Ponder, *A.* 223, 138).

Properties.—Plates, apparently rectangular. It has an odour of coumarin and rhubarb and attacks the skin. Easily soluble in alcohol, ether, benzene, and chloroform, less in petroleum-ether. In conc. H_2SO_4 it forms an orange solution. Forms a crystalline compound with $NaHSO_3$, and a di-bromide $C_{10}H_{10}OBr_2$ [125°] crystallising in needles from alcohol.

Phenyl hydrazide $C_{16}H_{16}N_2$: [156°]; flat yellow needles; sol. hot alcohol, sl. sol. cold alcohol and ether, insol. water (Fischer, *B.* 17, 576; Knorr, *B.* 20, 1099).

Oxim Ph.CH:CH.C(NOH).CH_3. [116°]. (220°) at 100 mm. Forms a bromide, [145°]; and an acetyl derivative [91°] (Zelinsky, *B.* 20, 922).

Di-benzylidine-acetone PhCH:CH.CO.CH:CH.Ph. *Cinnamone. Di-styryl ketone.* [112°].

Formation.—From benzoic aldehyde (20 pts.), acetone (6 pts.), and acetic acid (40 pts.), by adding H_2SO_4 (30 pts.) at 0° or passing in HCl.

Preparation.—From benzoic aldehyde (10 g.), acetone (3 g.), water (100 g.) and dilute (10 per cent.) NaOH (20 g.) left 4 days in the cold; or from benzylidene-acetone (7 g.), benzoic aldehyde (5 g.), water (200 g.), alcohol (150 g.) and dilute NaOH (20 g.) (Claisen a. Ponder, *A.* 223, 142; *cf.* Claisen a. Claparède, *B.* 14, 350, 2460; Schmidt, *B.* 14, 1459).

Properties.—Bright yellow monoclinic tablets (from acetone or $CHCl_3$) $a:b:c = 4{\cdot}886:1:1{\cdot}378$ $\beta = 78°\ 43'$. Readily soluble in chloroform or acetone, less in ether or cold alcohol. Gives an orange solution in H_2SO_4.

Tetrabromide $C_{17}H_{14}OBr_4$: white needles [208°-211°].

BENZYLIDENE-DIACETONE-ALCAMINE $C_{13}H_{17}NO$ *i.e.*

$$\begin{array}{c} H_2C-CH(OH)-CH_2 \\ | \quad\quad\quad\quad | \\ (C_6H_5)HC-NH-C(CH_3)_2 \end{array} \quad (?)$$

Oxy-phenyl-di-methyl-tetra-hydro-pyridine. Thick colourless oil. Formed by reduction of an acid solution of benzylidene-di-acetonamine (*v.* p. 27) with sodium-amalgam.—B'HCl: small crystals, easily soluble in water and alcohol (Fischer, *B.* 16, 2236).

BENZYLIDENE-DI-ACETONINE *v.* p. 34.

BENZYLIDENE - ACETOPHENONE C_6H_5.CH:CH.CO.C_6H_5. *Phenyl styryl ketone. Phenyl cinnamenyl ketone. Benzylidene methyl phenyl ketone. Benzal-acetophenone.* [58°]. (347°-348°). Formed by passing HCl gas into a mixture of acetophenone and benzaldehyde; by adding H_2SO_4 to the two latter bodies diluted with acetic acid; by heating them with acetic anhydride to 170°; or by treating them with dilute NaOH (Claisen a. Claparède, *B.* 14, 2463; Claisen a. Ponder, *A.* 223, 148).

Preparation.—12 pts. of acetophenone are mixed with 10·5 pts. of benzaldehyde and 8 pts. of a 20 p.c. sodium methylate solution, and allowed to remain in the cold for a few days when the whole will have solidified to a crystalline mass; the yield is 90 p.c. of the theoretical (Claisen, *B.* 20, 657). Large trimetric tables. V. sol. chloroform, ether, benzene and CS_2, m. sol. alcohol, sl. sol. petroleum ether. On oxidation it gives benzoyl-formic and benzoic acids. On boiling with dilute acids it is decomposed into acetophenone and benzaldehyde. By reduction with HI and P it is converted into di-benzyl-methane. The HCl *addition product* C_6H_5.CO.CHCl.CH_2.C_6H_5. [120°] forms colourless trimetric plates, sparingly soluble in cold alcohol and ether. It is prepared by the addition of gaseous HCl to the ketone. The *di-bromide* C_6H_5.CO.CHBr.CHBr.C_6H_5 [157°] forms short colourless prisms sol. hot alcohol. Prepared by the addition of bromine to the ketone.

BENZYLIDENE - β - ACETYL - PROPIONIC ACID $C_{12}H_{12}O_3$ *i.e.* CHPh:CH_2.CO.CH_2.CH_2.CO_2H. *Benzylidene-lævulic acid. Cinnamoyl-propionic acid.* [120°-125°]. Formed by heating lævulic acid with benzoic aldehyde and sodium acetate. Small white crystals. The lead salt is insoluble. Dissolves in cold conc. H_2SO_4 with a red colouration. Boiling conc. KOH splits off benzaldehyde. Reduction in alkaline solution yields *benzyl-valero-lactone* $C_{12}H_{14}O_2$ which forms large prisms of melting-point [85°] (Erdmann, *B.* 18, 3441).

BENZYLIDENE-ISOAMYL-AMINE. An oil formed from benzoic aldehyde and isoamyl-amine (Schiff, *A.* 140, 93).

BENZYLIDENE DI-ISOAMYL DI-OXIDE $C_6H_5CH(OC_5H_{11})_2$. (292° cor.). From benzylidene chloride and $NaOC_5H_{11}$ (Wicke, *A.* 102, 363).

BENZYLIDENE - ANILINE $C_{13}H_{11}N$ *i.e.* C_6H_5.CH:NPh. *Anilide of benzoic aldehyde.* [49°] (Tiemann a. Piest, *B.* 15, 2028).

Formation.—1. By warming aniline with benzoic aldehyde (Laurent a. Gerhardt, *Compt. chim.* 1850, 117).—2. By heating di-phenyl-thio-urea with benzoic aldehyde (Schiff, *A.* 148, 336).

Properties.—Laminæ; volatile with steam, insol. water, v. e. sol. alcohol and ether. At 200° it changes to an isomeride which differs from it in forming a salt $B'_2H_2PtCl_6$.

Hydrocyanide $C_{14}H_{12}N_2$. [82°]. Formed by passing HCN into fused benzylidene-aniline, or by the action of KCN on a mixture of benzoic aldehyde and aniline hydrochloride dissolved

in alcohol (Cech, *B.* 11, 246). It forms concentric needles, insol. alkalis and dilute acids.

BENZYLIDENE-DI-ANTIPYRINE *v.* DI-OXY-TETRA-METHYL-DI-QUINIZYL-PHENYL-METHANE.

DI-BENZYLIDENE-BENZIDINE $C_{26}H_{20}N_2$ *i.e.* $C_{12}H_8(N:CHPh)_2$. [232°] (C.); [239°] (B.). Obtained by heating hydrazo-benzene or benzene-azo-benzene with benzoic aldehyde and $ZnCl_2$ (Clève, *Bl.* [2] 45, 188; Barzilovsky, *J. R.* 1885, 366). Yellow scales (from benzene and chloroform). Resolved by HCl into benzoic aldehyde and benzidine.

BENZYLIDENE-DI-BENZAMIDE $C_{21}H_{18}N_2O_2$ *i.e.* $C_6H_5.CH(NH.CO.C_6H_5)_2$. [197°]. Formed by heating benzoic aldehyde with benzamide (Roth, *A.* 154, 76). Long silky needles (from alcohol), insol. water. Resolved by hot HClAq into the parent substances.

BENZYLIDENE DI-BENZOATE $C_6H_5.CH(OBz)_2$. From benzylidene chloride and AgOBz (Engelhardt, *J.* 1857, 471). Crystalline.

BENZYLIDENE-BENZYL-AMINE $C_6H_5.CH:N.CH_2.C_6H_5$. (c. 300°). Formed by the action of PCl_5 upon di-benzyl-hydroxylamine, probably by intermediate formation of the chloride $(C_6H_5.CH_2)_2N.Cl$. Oil. V. sol. alcohol and ether, insol. water.

Salts. B'HCl: [251°]; long plates or tables; v. sol. alcohol, sparingly in cold water, more readily in hot. $B'_2H_2PtCl_6$: small golden-yellow crystals (Walder, *B.* 19, 1632).

BENZYLIDENE BROMIDE $C_7H_6Br_2$ *i.e.* $C_6H_5.CHBr_2$. *Benzal bromide. ω-Di-bromo-toluene.* (130°–140°) at 20 mm. From benzoic aldehyde and PBr_5. Can only be distilled *in vacuo*. Sodium at 180° forms toluene and di-benzyl (Michaelson a. Lippmann, *Bl.* [2] 4, 251).

BENZYLIDENE BROMIDE BENZOATE $C_{14}H_{11}BrO_2$ *i.e.* $C_6H_5.CH{<}^{Br}_{O.CO.C_6H_5}$. [70°]. Colourless tables or prisms. Sol. alcohol, ether, and acetic acid. Prepared by mixing benzaldehyde and benzoyl bromide. On distillation it again decomposes into these bodies (Claisen, *B.* 14, 2475; *cf.* Liebig u. Wöhler, *A.* 3, 266).

BENZYLIDENE-DI-BUTYRAMIDE $C_{15}H_{22}N_2O_2$ *i.e.* $C_6H_5.CH(NH.CO.C_3H_7)_2$. Slender crystals formed by heating butyramide with benzoic aldehyde (Strecker, *A.* 154, 76).

BENZYLIDENE-DI-CARBAMIC ACID $C_6H_5.CH(NH.CO_2H)_2$.

Ethyl ether Et_2A''. [171°]. From carbamic ether, benzoic aldehyde, and HCl (Bischoff, *B.* 7, 631). Crystals; may be sublimed.

Propyl ether Pr_2A''. [143°] (Bischoff, *B.* 7, 1082).

BENZYLIDENE-CHLORAL-AMMONIA $C_9H_8Cl_3NO$ *i.e.* $CCl_3.CH(OH).N:CH.C_6H_5$. [130°]. White leaflets. Decomposed by dilute acids and by boiling water. Prepared by the action of benzoic aldehyde on chloral ammonia (Schiff, *B.* 11, 2166).

BENZYLIDENE CHLORIDE $C_7H_6Cl_2$ *i.e.* $C_6H_5.CHCl_2$. *Benzal chloride. Chlorobenzol. Benzylene chloride.* Mol. w. 161. (204°) at 756 mm. S.G. $\frac{0}{0}$ 1·27. S.V. 154·25 (Schiff, *B.* 19, 563).

Formation.—1. From benzoic aldehyde and PCl_5 (Cahours, *A.* 70, 39; *Suppl.* 2, 253, 306).—2. By passing chlorine into boiling toluene (Beilstein, *A.* 116, 336; 146, 322; Lauth a. Grimaux, *Bl.* 2, 347).—3. From benzoic aldehyde and succinyl chloride (Rembold, *A.* 138, 189) or $COCl_2$ (Kempf, *Z.* 1871, 79).

Preparation.—1. By passing 2 mols. of chlorine into cold toluene (1 mol.) exposed to direct sunshine (Schramm, *B.* 18, 608).—2. By heating toluene (7 pts.) with PCl_5 (30 pts.) at 190°; the yield being nearly that calculated (Colson a. Gautier, *Bl.* [2] 45, 87).

Properties.—Oil, with faint odour.

Reactions.—1. Converted into benzoic aldehyde by *water* or aqueous K_2CO_3 at 130°, or by warming with H_2SO_4 at 50° and treating the product with water (Oppenheim, *B.* 2, 213).—2. Alcoholic KHS forms benzyl disulphide and di-thio-benzoic acid.—3. Red-hot *soda lime* forms benzene (Limpricht, *Bl.* 1866, ii. 467).—4. *Chlorine* forms *p*-chloro-benzylidene chloride. 5. *Nitric acid* forms *p*-nitro-benzylidene chloride (Hübner a. Bente, *B.* 6, 803; *cf.* Beilstein, *A.* 146, 333).—6. AgOAc forms $C_6H_5.CH(OAc)_2$. 7. *Silver oxalate* forms benzoic aldehyde (Golowkinsky, *A.* 111, 252).—8. Na forms di-phenyl-ethylene.—9. MeI and Na form cumene.—10. NH_3 forms hydrobenzamide.—11. $ZnEt_2$ diluted with benzene forms $C_{11}H_{16}$ di-ethyl-phenyl-methane and $C_{22}H_{30}$ (Dafert, *M.* 4, 618). 12. *Copper* at 100° gives $CPhCl_2.CPhCl_2$ and CPhHCl.CPhHCl (Onufrowicz, *B.* 17, 833).

BENZYLIDENE-DI-CHLORO-CHROMIC ACID *v.* TOLUENE.

DI-BENZYLIDENE-ETHYLENE-DIAMINE $C_{16}H_{16}N_2$ *i.e.* $C_2H_4(N:CH.C_6H_5)_2$. [54°]. Formed by heating ethylene-diamine (1 mol.) with benzoic aldehyde (2 mols.) to 120°. Large colourless tables. V. sol. alcohol and benzene, insol. water. Decomposed into its constituents by acids (Mason, *B.* 20, 270).

BENZYLIDENE-ETHYLENE-DI-SULPHIDE

$$C_6H_5.CH{<}\begin{matrix}S.CH_2\\ |\\ S.CH_2\end{matrix}.$$

[29°]. Formed by passing HCl gas into a mixture of equal mols. of benzaldehyde and ethylene sulphydrate. Crystals. Easily soluble in alcohol, ether, and benzene, insoluble in water. Very stable body. By the action of bromine upon the chloroform solution di-ethylene-tetra-sulphide $C_2H_4{<}^{S_2}_{S_2}{>}C_2H_4$ is formed (Fasbender, *B.* 20, 460).

BENZYLIDENE-DI-ETHYL-DI-OXIDE $C_6H_5.CH(OEt)_2$. (222° cor.) *Diethyl derivative of benzoic ortho-aldehyde.* From benzylidene chloride and NaOEt (Wicke, *A.* 102, 363).

BENZYLIDENE-DI-HEPTYLENE-TETRA-UREA $C_{23}H_{40}N_8O_4$ *i.e.* $C_6H_5.CH(NH.CO.NH.C_7H_{14}.NH.CO.NH_2)_2$. From benzoic aldehyde and heptylene-diurea (Schiff, *A.* 151, 195). Insoluble powder.

BENZYLIDENE-MALONIC ACID $Ph.CH:C(CO_2H)_2$. [196°] (C.); [193°] (S.).

Formation.—1. From the ether by aqueous baryta.—2. From benzoic aldehyde, malonic acid and Ac_2O at 100° (Claisen a. Crismer, *A.* 218, 135).—3. From benzoic aldehyde, sodic malonate, and glacial acetic acid at the ordinary temperature: $Ph.CHO + CH_2(CO_2Na)_2 = PhCH:C(CO_2Na)_2 + H_2O$. The product is diluted with water, shaken out

with ether, acidified, shaken again with ether and the ether distilled off (Stuart, *C. J.* 43, 405; *v.* also Claisen, *A.* 218, 129).

Properties.—Colourless glassy prisms. Sl. sol. cold water, v. e. sol. hot water, v. sol. alcohol, acetic ether or acetone, m. sol. ether or glacial acetic acid. Insol. benzene, chloroform or petroleum. Does not give in neutral solutions a pp. with $BaCl_2$; but on warming such a mixture needles of the salt BaA″ separate (characteristic reaction).

Salt.—Ag_2A''.

Reactions.—1. At 200° it splits up into CO_2 and cinnamic acid.—2. Boiling *water* decomposes it into benzoic aldehyde and malonic acid, some CO_2 and cinnamic acid being also formed. 3. Reduced by *sodium amalgam* to benzyl malonic acid $Ph.CH_2.CH(CO_2H)_2$.—4. *Bromine* acts on its solution in chloroform forming $PhCHBr.CBr(CO_2H)_2$ [96°] whence water forms a-bromo-cinnamic acid (Stuart, *C. J.* 49, 360).—5. Cold *alcoholic potash* forms crystals of $Ph.CH(OEt)CH(CO_2K)_2$, whence a silver salt, $PhCH(OEt)CH(CO_2Ag)_2$ may be got. The free acid, if heated rapidly, melts at 120°-130°, splitting up into EtOH and benzylidene-malonic acid, which then solidifies again, and melts a second time at 190°. By crystallisation from water the acid is partly split up into alcohol and benzylidene-malonic acid.—6. HBr forms β-bromo-phenyl-isosuccinic acid $Ph.CHBr.CH(CO_2H)_2$, which is decomposed by water into HBr, cinnamic acid and CO_2 (Stuart, *C. J.* 49, 360).

Ethyl ether Et_2A''. [32°]. (192°) at 17mm. S.G. $\frac{15}{15}$ 1·111. Formed by passing HCl into a mixture of malonic ether and benzoic aldehyde or by treating the mixture with Ac_2O at 160° (Claisen, *B.* 14, 348). Large transparent crystals (Stuart, *C. J.* 49, 360). Boils at 308°-312° with decomposition.

BENZYLIDENE-MESITYL-OXIDE $C_{13}H_{14}O$ *i.e.* $(CH_3)_2C:CH.CO.CH:CH.C_6H_5$. (179°) at 14 mm. Oil. Prepared by passing HCl gas into a mixture of mesityl oxide and benzaldehyde (Claisen, *B.* 14, 351). Forms a tetrabromide [118°].

BENZYLIDENE-METHYL-KETOLE $C_{25}H_{22}N_2$ [248°]. Colourless plates. Formed by reduction of dimethyl-rosindole $C_{25}H_{20}N_2$ with zinc-dust and NH_3. It is oxidised in acetic acid solution by Fe_2Cl_6 back to di-methyl-rosindole (Fischer a. Wagner, *B.* 20, 816).

BENZYLIDENE-DI-METHYL-DI-OXIDE $C_6H_5CH(OMe)_2$. *Di-methyl derivative of benzoic orthoaldehyde.* (208° cor.). From benzylidene chloride and NaOMe (Wicke, *A.* 102, 363).

BENZYLIDENE-DI-METHYL-*p*-PHENYLENE-DIAMINE $C_6H_5.CH:N.C_6H_4.NMe_2$. *Benzylidene-amido-di-methyl-aniline. Methyl-phenylene-diamide of benzoic aldehyde* [98°]. Glistening plates or needles. Sol. hot alcohol and benzene, sl. sol. cold alcohol. Weak base. Formed by mixing benzoic aldehyde and *u*-di-methyl-*p*-phenylene-diamine, either directly or in alcoholic solution. By HCl it is split up into its generators.—$B''H_2Cl_2$: white solid (Calm, *B.* 17, 2940).

BENZYLIDENE-(*Py.* 3)-METHYL-QUINOLINE $C_{17}H_{13}N$ *i.e.*

$$C_6H_4\begin{cases}CH:CH\\ \quad\ \ |\\ N:C-CH=CH.C_6H_5(?)\end{cases}$$

[100°]. Formed by heating quinaldine (methyl-quinoline) with benzoic aldehyde or benzylidene chloride and $ZnCl_2$ (Jacobsen a. Reimer, *B.* 16, 2606). Glistening colourless needles. Sublimable. Sol. hot alcohol, insol. water.—$B'H_2Cr_2O_7$ 2½aq: very sparingly soluble reddish-yellow needles.

BENZYLIDENE-(β)-NAPHTHYLAMINE $C_6H_5.CH:N.C_{10}H_7$. [103°]. From benzoic aldehyde and (β)-naphthylamine (Claisen, *A.* 237, 261).

BENZYLIDENE-(α)-NAPHTHYLAMINE-*p*-SULPHONIC ACID $C_{10}H_6(N:CH.C_6H_5).SO_3H[1:4]$. The sodium salt (A′Na) is obtained by shaking a strong solution of sodium-(α)-naphthylamine-sulphonate with benzaldehyde. By long boiling with water it is split up into its constituents (Cahn a. Lange, *B.* 20, 2001).

BENZYLIDENE-DI-(β)-NAPHTHYL-OXIDE $C_6H_5.CH\langle{}^{C_{10}H_6}_{C_{10}H_6}\rangle O$. *Anhydride of di-oxy-di-naphthyl-phenyl-methane.* [190°]. Crystalline solid. Insoluble in aqueous alkalis.

Formation.—1. By heating a solution of (β)-naphthol and benzoic aldehyde in acetic acid to 200°, or with addition of H_2SO_4 or HCl on the water-bath (Trzcinski, *B.* 17, 499).—2. By warming benzylidene di-naphthyl di-oxide $C_6H_5.CH(O.C_{10}H_7)_2$ with acetic acid and a few drops of HCl. In these reactions di-oxy-di-naphthyl-phenyl-methane $C_6H_5.CH(C_{10}H_6.OH)_2$ must first be formed and at once split off H_2O (Claisen, *B.* 19, 3317).

Benzylidene-di-(β)-naphthyl-di-oxide $C_{27}H_{20}O_2$ *i.e.* $C_6H_5.CH(OC_{10}H_7)_2$. *Di-naphthyl ortho-benzaldehyde.* [205°]. From benzoic aldehyde (5·3 pts.), (β)-naphthol (7·2 pts.), glacial HOAc (30 pts.), and fuming HCl (2 pts.) at 0° (Claisen, *A.* 237, 269). Tables, sl. sol. $CHCl_3$ and CS_2, v. sl. sol. alcohol and ether, insol. alkalis. Conc. H_2SO_4 gives, on gentle warming, a deep-red solution. HOAc and some HCl slowly convert it at 100° into benzylidene-di-naphthyl oxide, a change which also occurs when it is heated at 210°.

BENZYLIDENE OXAMIDE $C_9H_8N_2O_2$. Formed by warming oxamic ether with benzoic aldehyde (Medicus, *A.* 157, 60). Laminæ.

BENZYLIDENE-PHENYL-DIAMINE *v.* Phenyl-benzamidine.

DI-BENZYLIDENE-*p*-PHENYLENE DI-AMINE $C_{20}H_{16}N_2$ *i.e.* $C_6H_4(N:CHPh)_2$. [140°]. From *p*-phenylene-diamine and benzoic aldehyde at 120° (Ladenburg, *B.* 11, 590). Plates (from alcohol). Resolved by hot HClAq into the parent substances.

BENZYLIDENE-PHTHAL-ETHYL-IMIDINE $C_{17}H_{15}ON$ *i.e.* $C_6H_4\langle{}^{C(=CH.C_6H_5)}_{CO}\rangle NEt$. *Ethyl-phthalimyl-benzyl.* [c. 77°]. Formed by boiling the ethyl-amide of deoxybenzoïn-o-carboxylic acid $C_6H_4(CO.NHEt)CO.CH_2.C_6H_5$ with acetic acid. Plates. V. sol. alcohol, benzene, benzoline, and CS_2 (Gabriel, *B.* 18, 2433).

BENZYLIDENE-PHTHALIDE $C_{15}H_{10}O_2$ *i.e.* $C_6H_4\langle{}^{C:(CHPh)}_{CO}\rangle O$. [99°]. *Benzylidene-phthalyl. Anhydride of deoxybenzoïn carboxylic acid.*

Formation.—1. By heating phthalic anhydride (5 pts.) with phenyl-acetic acid (5 pts.) and NaOAc (1 pt.) (Gabriel a. Michael, *B.* 11, 1018).

3. By heating phthalyl-phenyl-acetic acid *in vacuo* (Gabriel, *B.* 17, 2526).

Preparation.—A mixture of 100 g. phenyl-acetic acid, 110 g. phthalic anhydride and 2½ g. dry sodium acetate is heated for 2 hours, and the product crystallised from alcohol; the yield is 75-78 p.c. (Gabriel, *B.* 18, 3470).

Properties.—Long prisms (from alcohol); insol. water, sl. sol. cold alcohol.

Reactions.—1. Hot aqueous KOH forms potassium deoxybenzoïn carboxylate.—2. By heating with alcoholic NH_3 at 100° it is converted into deoxybenzoïn - carboxylamide $C_6H_4<\genfrac{}{}{0pt}{}{CO.CH_2.C_6H_5}{CO.NH_2}$, which by solution in H_2SO_4 or by boiling with glacial acetic acid loses H_2O giving benzylidene-phthalimidine (phthalimidyl-benzyl) $C_6H_4<\genfrac{}{}{0pt}{}{C(:CH.C_6H_5)}{CO}>NH$. —3. Similarly *ethyl-amine* yields the ethyl-amide of deoxybenzoïn-carboxylic acid, and this on boiling with acetic acid gives benzylidene-phthal-ethyl-imidine $C_6H_4<\genfrac{}{}{0pt}{}{C(:CH.C_6H_5)}{CO}>NEt$ (Gabriel, *B.* 18, 2433).—4. By dissolving in benzene and treatment with *nitrous acid gas* it yields the compound $C_6H_4<\genfrac{}{}{0pt}{}{C(NO_2).(CH(NO_2).C_6H_5)}{CO}>O$ (Gabriel, *B.* 18, 1251).

References.—*V.* CYANO- and NITRO-BENZYLIDENE-PHTHALIDE.

Benzylidene-phthalide-di-bromide

$C_6H_4<\genfrac{}{}{0pt}{}{CBr(-CHBr.C_6H_5)}{CO}>O$. [146°]. Formed by the combination of benzylidene-phthalide with bromine (Gabriel, *B.* 17, 2527). Thick glistening prisms. Sparingly soluble in alcohol.

(*Iso*)-**Benzylidene-phthalide** $C_{15}H_{10}O_2$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CH:C.C_6H_5}{CO.O}$. [91°]. Formed by reduction of nitro-benzylidene-phthalide $C_6H_4<\genfrac{}{}{0pt}{}{C(-C(NO_2).C_6H_5)}{CO}>O$ with HI and P. Prepared by reduction of nitro-benzylidene-phthalide; yield, 47 p.c. of the phenyl-acetic acid employed to prepare the benzylidene-phthalide (Gabriel, *B.* 18, 3471). Flat colourless needles. Easily soluble in alcohol and benzene, sparingly in ligroïn. By further reduction with HI and P at 200° it yields *s*-di-phenyl ethane *o*-carboxylic acid $C_6H_4(CH_2.CH_2.C_6H_5).CO_2H$. By boiling with aqueous NaOH it is converted into deoxybenzoïn - *o* - carboxylic acid $C_6H_4(CO_2H).CH_2.CO.C_6H_5$. Heated with alcoholic NH_3 it gives isobenzylidene phthalimidine $C_6H_4<\genfrac{}{}{0pt}{}{CH:C.C_6H_5}{CO.NH}$ (Gabriel, *B.* 18, 2445).

BENZYLIDENE-PHTHAL-IMIDINE

$C_{15}H_{11}ON$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{C:CH.C_6H_5}{CO}>NH$. *Phthalimidyl-benzyl.* [183°]. Yellow plates. Formed from the amide of deoxybenzoïn-*o* carboxylic acid $C_6H_4(CO.NH_2).CO.CH_2.C_6H_5$ by solution in H_2SO_4 or by boiling with acetic acid (Gabriel, *B.* 18, 2433). *V.* also BROMO- and NITRO-BENZYLIDENE PHTHALIMIDINE.

Isobenzylidene-phthalimidine *v.* (*Py.* 4)-OXY-(*Py.* 2)-PHENYL-ISOQUINOLINE.

BENZYLIDENE-DI-PIPERIDINE

$C_6H_5.CH(C_5H_{10}N)_2$. [81°]. Formed by heating piperidine with benzoic aldehyde. Colourless prisms. Very unstable, being decomposed even by boiling with water. Dilute acids resolve it into benzoic aldehyde and piperidine (Laun, *B.* 17, 678).

BENZYLIDENE-RHODANIC ACID

$C_{10}H_7NS_2O$ *i.e.* $C_6H_5.CH:C(SH).CO.S.CN$. [200°]. Formed by the action of benzoic aldehyde upon rhodanic acid in presence of dehydrating agents (Nencki, *B.* 17, 2278). Yellow needles, sol. water. By heating with baryta-water it is split up into α-sulphydro-cinnamic acid $C_6H_5.CH:C(SH).CO_2H$ and hydrogen sulphocyanide. Heated at 410° with conc. H_2SO_4 (4 pts.) it is converted into benzylidene-rhodanic-oxy-sulphonic acid $C_{10}H_7NS_2O_5$ (Ginsburg a. Bondzynski, *B.* 19, 119).

BENZYLIDENE-RHODANIC-OXY-SULPHONIC ACID $C_{10}H_7NS_2O_5$. Formed by heating benzylidene-rhodanic acid with conc. H_2SO_4 (4 pts.) at 110°. Needles. V. sol. water and alcohol. Very strong acid (Ginsburg a. Bondzynski, *B.* 19, 119).

BENZYLIDENE - ROSANILINE $C_{27}H_{23}N_3$. From rosaniline and benzoic aldehyde by heat or by shaking with SO_2Aq (Schiff, *A.* 140, 111; *Z.* 1867, 176).—$B'_2H_2PtCl_6$.

BENZYLIDENE SELENIDE C_6H_5CHSe. *Seleno-benzoic aldehyde.* [70°]. From benzylidene chloride and alcohol K_2Se (Cole, *B.* 8, 1165). Yellow needles (from alcohol), insol. water. Not attacked by NH_3.

BENZYLIDENE-DI-SKATOLE $C_{25}H_{22}N_2$ *i.e.* $PhCH(C_9H_8N)_2$. [142°]. From skatole (2½ pts.), benzoic aldehyde (1 pt.) and a little $ZnCl_2$ (Wenzing, *A.* 239, 241). Insol. water; v. sol. hot alcohol and ether. Boiling HCl does not split off benzoic aldehyde.

BENZYLIDENE SULPHIDE *v.* THIO-BENZOIC ALDEHYDE.

BENZYLIDENE THIO-BIURET $C_9H_9N_3S_2$ *i.e.* $C_6H_5.CH<\genfrac{}{}{0pt}{}{N:C(SH)}{N:C(SH)}>NH(?)$. [237°]. Formed by heating benzoic aldehyde with ammonium sulphocyanide at 137°-165° (Brodsky, *M.* 8, 27). Minute prisms (from alcohol); insol. water, sl. sol. cold alcohol; sol. dilute KOH. Boiling baryta-water forms benzoic aldehyde, barium sulphocyanide, and di-phenyl-thio-urea.

Acetyl derivative $C_9H_7Ac_2N_3S_2$. [189°].

BENZYLIDENE *o*-TOLUIDINE $C_{14}H_{13}N$ *i.e.* $C_6H_5.CH:N.C_6H_4.CH_3$ [1:2]. *Benzaldehyde o-toluide* (314°). From *o*-toluidine and benzoic aldehyde (Etard, *C. R.* 95, 730). Resolved by boiling water into its generators. By passing through a tube heated to dull redness it is converted into phenyl-indole $C_6H_4<\genfrac{}{}{0pt}{}{CH}{NH}>C.C_6H_5$ (Pictet, *B.* 19, 1063).

Benzylidene-*p*-toluidine

$C_6H_5.CH:N.C_6H_4.CH_3$ [1:4]. From benzoic aldehyde and *p*-toluidine at 100° (Schiff, *A.* 140, 96; Kohler, *A.* 241, 359; Mazzara, *G.* 10, 370). Melts below 100°, but changes at 160° into an *isomeride* [120°-125°].—$B'_2H_2PtCl_6$.

DI-BENZYLIDENE-TOLYLENE-DIAMINE

$C_{21}H_{18}N_2$ *i.e.* $C_6H_3Me(N:CHPh)_2$ [1:2:4] [122°-123°]. From benzoic aldehyde and tolylene-diamine at 100° (Schiff, *A.* 140, 98). Neutral

crystalline mass; at 140°-150° it gives amarine.

BENZYLIDENE-DI-UREA $C_9H_{12}N_4O_2$ *i.e.* $C_6H_5.CH(NH.CO.NH_2)_2$. *Benzaldehyde di-ureide* [195°]. Formed by adding benzoic aldehyde to an alcoholic solution of urea (Schiff, *A.* 151, 192). Crystalline powder, insol. water and ether, sol. alcohol.

Di-benzylidene-tri-urea $C_{17}H_{20}N_6O_3$. Powder, formed by heating urea with benzoic aldehyde.

Tri-benzylidene-tetra-urea $C_{25}H_{28}N_8O_4$. [c. 240°]. Powder, formed by heating benzylidene-di-urea with benzoic aldehyde.

BENZYLIDENE-DI-URETHANE *v.* BENZYLIDENE-DI-CARBAMIC ACID.

BENZYL-INDOLE $C_{15}H_{13}N$ *i.e.* $C_6H_4<\frac{CH}{NC_7H_7}>CH$. [44·5°]. From its carboxylic acid (*q. v.*) by heat. Yellowish needles (from alcohol). V. sol. benzene, light petroleum, chloroform and ether. Turns pine wood moistened with HCl yellow. Picrate forms red needles.

BENZYL-INDOLE CARBOXYLIC ACID $C_{16}H_{13}NO_2$ *i.e.* $C_6H_4<\frac{CH}{NC_7H_7}>C.CO_2H$. [195°, with decomposition]. Pyruvic acid combines at 16° with benzyl-phenyl-hydrazine, forming $CH_3.C(CO_2H):N.NPhC_7H_7$ whence HCl at 100° forms benzyl-indol-carboxylic acid (Antrick, *A.* 227, 362).

Properties.—Colourless needles (from glacial acetic acid). Sl. sol. water, chloroform, and petroleum, sol. ether and alcohol, v. sl. sol. benzene. Converted by heat into CO_2 and benzyl indole.

BENZYL IODIDE C_7H_7I *i.e.* $C_6H_5CH_2I$. [24°]. S.G. $\frac{25}{}$ 1·73.

Formation.—1. From benzyl alcohol in CS_2 and iodide of phosphorus.—2. Slowly formed by the action of cold HI (S.G. 1·96) on benzyl chloride (Lieben, *Z.* [2] 6, 736).—3. From benzyl chloride and KI (V. Meyer, *B.* 10, 311; Kumpf, *A.* 224, 126), ZnI_2, or PbI_2 (Brix, *A.* 225, 154).

Properties.—Crystals: decomposed by distillation. Gives benzyl acetate with AgOAc, and tribenzylamine with alcoholic NH_3. Silver nitrite gives benzoic aldehyde and acid (Van Renesse, *B.* 9, 1454; Brunner, *B.* 9, 1744).

BENZYL-(*pseudo*)-ISATIN $C_{15}H_{11}NO_2$ *i.e.* $C_6H_4<\frac{CO}{NC_7H_7}>CO$. [131°]. From benzyl-indole carboxylic acid and NaOCl in feebly alkaline solution, the insoluble chloride then produced being subsequently boiled with alcoholic NaOH (Antrick, *A.* 227, 365).

Properties.—Slender needles (from alcohol). Sl. sol. water, sol. ether. Shows the indophenine reaction with H_2SO_4 and crude benzene containing thiophene.

DI-BENZYL-KETONE $C_{15}H_{14}O$ *i.e.* $CO(CH_2Ph)_2$. *Di-phenyl-acetone.* Mol. w. 210. [30°]. (320°). Formed by the dry distillation of barium phenyl-acetate. Prisms. CrO_3 oxidises it to benzoic and acetic acids (Popoff, *B.* 6, 560). Reduced by HI at 180° to di-benzyl-methane (Graebe, *B.* 7, 1623).

BENZYL-MALONIC ACID $C_{10}H_{10}O_4$ *i.e.* $C_6H_5.CH_2.CH(CO_2H)_2$. *Phenyl-isosuccinic acid.* [117°].

Formation.—1. By saponification of its ether. 2. From benzylidene-malonic acid by sodium-amalgam.

Properties.—Triclinic crystals, sol. water, alcohol, and ether. Splits up at 180° into CO_2 and β-phenyl-propionic acid.

Ethyl ether Et_2A''. (300°). S.G. $\frac{15}{15}$ 1·08 (Conrad, *A.* 204, 174; *B.* 12, 752). Sodium benzyl-malonic ether is converted by iodine dissolved in ether into $C_6H_5CH_2.C(CO_2Et)_2$, which is converted by alcoholic KOH into ethoxy-benzyl-malonic ether (Bischoff a. Hausdörfer, *A.* 239, 110). Converted by alcoholic NH_3 into the amides $CH_2Ph.CH(CONH_2)_2$ [225°] and $CH_2Ph.CH(CO_2Et)(CONH_2)$ [98°] (Bischoff a. Siebert, *A.* 239, 96).

Di-benzyl-malonic acid $(C_6H_5.CH_2)_2C(CO_2H)_2$. [172°]. P.; [163°] (B. a. H). Formed by saponifying the ether (Perkin, *C. J.* 47, 821). Slender needles (from water) or thick prisms (from alcohol). V. e. sol. ether and alcohol, m. sol. hot water, sl. sol. hot ligroïn. Gives di-benzyl-acetic acid on heating.

Ethyl ether $(C_6H_5.CH_2)_2C(CO_2Et)_2$. (250°) at 40 mm. S.G. $\frac{20}{}$ = 1·093. Thick yellow liquid. Formed by the action of benzyl chloride upon sodio-malonic ether. By heating with alcoholic KOH it is converted into di-benzyl-acetic acid (Lellmann a. Schleich, *B.* 20, 439). Converted by treatment with alcoholic ammonia into $CO_2Et.CH(C_7H_7).CO.NH_2$ and $(CO.NH_2)_2CH.CH_2Ph$, benzyl being split off (Bischoff a. Siebert, *A.* 239, 97).

TRI-BENZYL-MELAMINE $(C_6H_5.CH_2.NH.CN)_3$. Formed spontaneously from benzyl-cyanamide by isomeric change (Strakosch, *B.* 5, 694).—B'''3HCl.

BENZYL-MERCAPTAN C_7H_8S *i.e.* $C_6H_5.CH_2.SH$. Mol. w. 124. (195°). S.G. $\frac{20}{}$ 1·058. From benzyl chloride and KHS in alcohol (Märcker, *A.* 136, 75; 140 86) Pungent liquid with alliaceous odour.

Salts.—$(C_7H_7S)_2Hg$: needles.—C_7H_7SHgCl. —$(C_7H_7S)_2Pb$.

Benzoyl derivative $C_6H_5.CH_2.SBz$. [40°]. Colourless crystals (Otto a. Lüders, *B.* 13, 1285).

Ethyl derivative C_7H_7SEt. (216°).

BENZYL-MESITYLENE $C_{16}H_{18}$ *i.e.* $C_6H_5.CH_2.C_6H_2Me_3$. [36°]. (c. 302). V.D. 7·35. Prepared by boiling benzyl chloride with mesitylene in presence of Al_2Cl_6 (Louise, *A. Ch.* [6] 6, 176, *C. R.* 95, 1163). Prisms; v. sol. alcohol, ether, and benzene.

Reactions.—1. HI at 180° gives toluene and mesitylene.—2. CrO_3 gives benzoyl-mesitylene. 3. HNO_3 forms a tri-nitro-derivative, [185°] and an acid [266°].—4. Passage through a red-hot tube forms two di-methyl-anthracenes, anthracene, and phenanthrene.

Di-benzyl-mesitylene $(C_6H_5.CH_2)_2C_6HMe_3$. [131°]. (355°) at 120 mm. From benzyl-mesitylene, benzyl chloride, and Al_2Cl_6 (Louise, *A. Ch.* [6] 6, 197). Minute prisms.

BENZYL-METHANE *v.* ETHYL-BENZENE.

Di-benzyl-methane *v.* DI-PHENYL-PROPANE.

BENZYL MUSTARD OIL *v.* BENZYL THIO-CARBIMIDE.

BENZYL-METHYL-ACETIC ACID *v.* PHENYL-ISO-BUTYRIC ACID.

BENZYL-METHYL-ACETO-ACETIC ACID *v.* p. 25.

BENZYL-DI-METHYL-AMINE $C_9H_{13}N$ *i.e.* $C_6H_5.CH_2NMe_2$. *Di-methyl-benzylamine.* (184°). From benzyl chloride and alcoholic dimethylamine (Schotten, *B.* 15, 424; Jackson a. Wing, *Am.* 9, 78). Oil, miscible with alcohol and ether.

Salts.—*B'HCl.—*$B'HNO_3$.—$B'_2H_2PtCl_6$.—$B'_2H_4FeCy_6$.—$B'_2H_2ZnCl_4$.

Methylo-chloride B'MeCl: white crystals, sol. water, v. sl. sol. Na_2CO_3Aq.—$(B'MeCl)_2PtCl_4$.

BENZYL-TETRA-METHYL-BENZENE $C_6H_5.CH_2.C_6HMe_4$ [1:2:3:4:6]. [61°]. (c. 310°). From benzoyl-iso-durene and fuming HI at 250° (Essner a. Gossin, *Bl.* [2] 42, 170; *A. Ch.* [6] 1, 516).

BENZYL-METHYL-CARBINOL $C_6H_5.CH_2.CH(OH).CH_3$. (215° i. V.). From benzyl methyl ketone and sodium-amalgam (Errera, *G.* 16, 315).

BENZYL-METHYL-GLYOXIM $C_{10}H_{12}N_2O_2$ *i.e.* $C_6H_5.CH_2.C(NOH).C(NOH).CH_3$. [181°]. Formed by the action of hydroxylamine hydrochloride on isonitroso-benzyl-acetone (Schramm, *B.* 16, 180). Small white needles. Sol. alcohol and ether. Sublimable. Weak acid.

Di-acetyl-derivative $C_{10}H_{10}(NOAc)_2$—[80°], small white crystals (Schramm, *B.* 16, 2188).

BENZYL-METHYL-KETONE $C_9H_{10}O$ *i.e.* $C_6H_5.CH_2.CO.CH_3$ *Phenyl-acetone.* (215°). S.G. ^{0} 1·010. Produced, together with acetone and di-benzyl-ketone, by distilling calcium acetate with calcium phenyl-acetate (Otto, *J. pr.* [2] 1, 144). Unites with $NaHSO_3$. By heating with conc. H_2SO_4 on the water-bath it is converted into the sulphonic acid $C_6H_4(SO_3H).CH_2.CO.CH_3$; but by heating quickly to a higher temperature it is split up into ω-toluene-sulphonic acid $C_6H_5.CH_2.SO_3H$ and acetic acid (Krekeler, *B.* 19, 2625).

BENZYL-METHYL-KETONE SULPHONIC ACID $C_6H_4(SO_3H).CH_2.CH_2.CO.CH_3$. Formed by the action of fuming sulphuric acid upon benzyl methyl ketone in the cold.—PbA'_2 (Krekeler, *B.* 19, 2625).

BENZYL-METHYL-MALONIC ACID $C_{11}H_{12}O_4$ *i.e.* $C_6H_5CH_2.CMe(CO_2H)_2$. [135°]. Colourless crystals. Prepared from the ether. On heating it gives CO_2 and phenyl-iso-butyric acid.

Di-ethyl-ether $A''Et_2$. (300°). S.G. $\frac{15°}{15°}$= 1·064. Prepared by the action of benzyl chloride on sodio-methyl-malonic ether or of methyl iodide on sodio-benzyl-malonic ether (Conrad a. Bischoff, *B.* 13, 598; *A.* 204, 177).

BENZYL-METHYL OXIDE $C_6H_5.CH_2.O.CH_3$. (170°). From benzyl chloride and KOMe (Cahours, *C. R.* 80, 1317).

BENZYL-METHYL-PIPERIDINE $C_5H_9N(C_7H_7)(CH_3)$. (245°). Colourless fluid. Formed by dry distillation of the alkaline hydrate produced by the action of moist Ag_2O on benzyl-piperidine-methylo-iodide.—$(B'HCl)_2PtCl_4$ (Schotten, *B.* 15, 423).

DI-BENZYL-METHYL-(pseudo)-THIO-UREA $C_{16}H_{18}N_2S$ *i.e.* $CH_3.S.C{\lt}^{NC_7H_7}_{NHC_7H_7}$. Formed by heating di-benzyl-thio-urea with methyl iodide at 100°. Oil. V. sol. alcohol and ether, insol. water.

Salts.—B'HCl: [120°]; easily soluble large rhombic four-sided tables.—$B'H_2SO_4$: [145°]; glistening needles; v. sol. water and alcohol.—B'HI: [99°]; octahedra; v. sol. warm alcohol, sl. sol. hot water.—$B'_2H_2Cl_2PtCl_4$: sparingly soluble four-sided prisms (Reimarus, *B.* 19, 2348).

(α)-BENZYL-NAPHTHALENE $C_{17}H_{14}$ *i.e.* $C_6H_5.CH_2.C_{10}H_7$. [59°]. (c. 330°). S.G. ^{17} 1·166. S. (alcohol) 3·3 at 78°; S. (ether) 50 at 15°. From naphthalene, benzyl chloride, and zinc-dust (Froté, *C. R.* 76, 639; Miquel, *Bl.* [2] 26, 2). Monoclinic prisms. Dilute HNO_3 produces phenyl (α)-naphthyl ketone [75°].

Sulphonic acid $C_{17}H_{13}SO_3H$.—KA' aq: needles (from alcohol).

(β)-**Benzyl-naphthalene** $C_{17}H_{14}$. [55°]. (c. 345°). S.G. ^{0} 1·176. S. (alcohol) 2·25 at 15°. Formed, together with the preceding, by heating naphthalene with benzyl chloride and Al_2Cl_6 (Vincent a. Roux, *Bl.* [2] 40, 163). Monoclinic prisms (from alcohol); v. e. sol. benzene and chloroform. Nitric acid produces phenyl (β)-naphthyl ketone [82°].

BENZYL-(α)-NAPHTHYLAMINE $C_6H_5.CH_2.NH.C_{10}H_7$. [67°]. From naphthylamine and benzyl chloride (Froté a. Tommasi, *Bl.* [2] 20, 67).

BENZYL-NAPHTHYL-KETONE $C_{18}H_{14}O$ *i.e.* $C_{10}H_7$—CO—$CH_2.C_6H_5$. [57°]. Tables. Prepared by the action of Al_2Cl_6 on a mixture of phenyl-acetyl chloride and naphthalene. On reduction with HI it gives phenyl-naphthyl-ethane (Graebe a. Bungener, *B.* 12, 1078).

BENZYL-NAPHTHYL-METHANE *v.* PHENYL-NAPHTHYL-ETHANE.

BENZYL-(β)-NAPHTHYL OXIDE $C_6H_5.CH_2.O.C_{10}H_7$. [99°]. White plates. Prepared by the action of benzyl chloride on sodium-(β)-naphthol (Staedel, *B.* 14, 899; *A.* 217, 47).

BENZYL-NARCEÏNE *v.* NARCEÏNE.

BENZYL-NITRATE $C_6H_5.CH_2.NO_3$. Is perhaps formed by the action of benzyl chloride on $AgNO_3$ (Brunner, *B.* 9, 1745).

BENZYL-NITRO-ARBUTIN *v.* p. 298.

BENZYL-NITRO-PHENYL- *v.* NITRO-PHENYL-BENZYL-.

BENZYL-ISO-NITROSO-MALONIC ACID $C_6H_5.CH_2.ON:C:(CO_2H)_2$. From its ether. The potassium salt on dry-distillation gives KCN, potassium carbonate and benzyl alcohol.

Di-ethyl ether $A''Et_2$. Prepared by the action of benzyl chloride and sodium ethylate on iso-nitroso-malonic ether (Conrad a. Bischoff, *B.* 13, 599).

BENZYL-NITROSO-MALONYL-UREA *v.* *Benzyl ether of* VIOLURIC ACID.

BENZYL-OXALATE $C_{16}H_{14}O_4$ *i.e.* $(C_6H_5.CH_2)_2C_2O_4$. [81°]. From benzyl chloride and silver oxalate (Beilstein a. Kuhlberg, *A.* 147, 341). Scales (from alcohol); may be distilled.

BENZYL OXAMATE $C_9H_9NO_3$ *i.e.* $NH_2.CO.CO_2.CH_2Ph$. [135°]. From $NH_2.CCl_2.CO_2.CH_2Ph$ and benzyl alcohol (Wallach a. Liebmann, *B.* 13, 507).

DI-BENZYL OXAMIDE $C_{16}H_{16}N_2O_2$ *i.e.* $C_2O_2(NH.CH_2Ph)_2$. [216°]. From oxalic ether and benzylamine; or by boiling benzylamine cyanide with HCl (Strakosch, *B.* 5, 694). Scales (from alcohol).

BENZYL-OXANTHRANOL *v.* OXANTHRANOL.

TETRA-BENZYL-OXY-AMMONIUM IODIDE v. HYDROXYLAMINE.

BENZYL-OXY-BENZOIC ACID v. OXY-BENZYL-BENZOIC ACID.

BENZYL-OXY-BUTYRIC ACID v. OXY-PHENYL-VALERIC ACID.

BENZYL-OXY-MALONIC ACID v. BENZYL-TARTRONIC ACID.

BENZYL-OXY-SULPHIDE v. DI-BENZYL SULPHOXIDE.

BENZYL - PHENANTHRENE $C_{21}H_{16}$ *i.e.* $CH_2Ph.C_{14}H_9$. [156°]. From benzyl chloride, phenanthrene (*q.v.*) and zinc-dust (Goldschmiedt, *M.* 2, 444). Needles (from benzene). CrO_3 gives benzoic acid and phenanthraquinone.

p - BENZYL - PHENOL $C_{13}H_{12}O$ *i.e.* $C_6H_5.CH_2.C_6H_4.OH$ [1:4]. *Oxy-di-phenyl-methane.* Mol. w. 184. [84°]. (325°–330°).

Formation.—1. From phenol, benzyl chloride and zinc-dust (Paterno, *G.* 2, 2; 3, 121).—2. From benzoyl-anisol and HI (Paterno, *B.* 5, 288; 6, 1202).—3. From PhOAc and $C_6H_5.CH_2Cl$ alone or with Al_2Cl_6, and saponification of the product (Perkin, jun., a. Hodgkinson, *C. J.* 37, 722; Rennie, *C. J.* 41, 228).—4. By heating phenol with benzyl alcohol and $ZnCl_2$ (Liebmann, *B.* 15, 152).—5. By diazotising *p*-amido-di-phenyl-methane and treating the product with water (Basler, *B.* 16, 2719).

Properties.—Long needles or plates (from alcohol). Sol. KOHAq but not NH_3Aq.

Reactions. — 1. Distilling with P_2O_5 gives benzene, phenol, and anthracene.—2. By *bromination* and *nitration*, or by nitration and bromination it gives the same bromo-nitro-derivative, when treated with HNO_3 in $C_2H_4O_2$ forms $C_6H_2(OH)(NO_2)_2Br$ [1:2:4:6]. Hence the bromo-nitro-derivative $C_6H_2(OH)(C_7H_7)(NO_2)Br$ is either [1:2:4:6] or [1:4:2:6]. But the oxidation of $C_6H_5.CH_2.C_6H_4OMe$ to $C_6H_5CO.C_6H_4OMe$ [1:4] shows that the arrangement is [1:2:4:6].—3. Phosphorus pentachloride forms $(C_{13}H_{11})_3PO_4$ [94°].—4. Chloro-acetic acid and KOH convert benzyl-phenol into $CH_2Ph.C_6H_4.O.CH_2.CO_2H$, [100°], while $CH_3.CHCl.CO_2H$ and KOH give rise to $CH_2Ph.C_6H_4.O.CHMe.CO_2H$ [102°] (Mazzara, *G.* 11, 437; 12, 262).

Methyl derivative $C_6H_5.CH_2.C_6H_4OMe$. *Benzyl-anisol.* (305°). From anisol, benzyl chloride, and zinc. Oxidised by alkaline $KMnO_4$ it gives the methyl derivative of *p*-benzoyl-phenol.

Acetyl derivative $Ph.CH_2.C_6H_4.OAc$. (315°–320°).

Benzoyl derivative $PhCH_2.C_6H_4.OBz$. [86°].

Sulphonic acid $C_7H_7.C_6H_3(SO_3H)(OH)$.

Salts.—NH_4A'aq: needles.—KA′: feathery crystals.—BaA'_2.—$C_{13}H_{10}SO_4Ba$ aq: minute crystals.—These salts are all sparingly soluble (Rennie, *C. J.* 41, 34; 49, 406). They, as well as the free acid, give a violet colour with Fe_2Cl_6.

p-BENZYL-DIPHENYL $C_{19}H_{16}$ *i.e.* $C_6H_5.CH_2.C_6H_4.C_6H_5$. [85°]. (286°) at 100 mm. By heating benzyl chloride and diphenyl with zinc dust at 100° two benzyl-diphenyls are produced together with traces of anthracene. The *p*-hydrocarbon is less soluble and solidifies more easily than its isomeride (Goldschmiedt, *M.* 2, 433). Leaflets or needles, m. sol. alcohol, v. sol. benzene and ether. CrO_3 oxidises it, to phenyl-benzophenone and benzophenone *p*-carboxylic acid.

o-Benzyl-diphenyl (?). [54°]. (c. 285°) at 110 mm. Prepared as above. Monoclinic needles. CrO_3 oxidises it completely.

Di-benzyl-diphenyl $C_{12}H_8(CH_2Ph)_2$. [118°]. From di-benzoyl-diphenyl and HI at 170° (Wolf, *B.* 14, 2032). Laminæ (from alcohol).

BENZYL-PHENYL- v. PHENYL-BENZYL-.

BENZYL-DIPHENYL-AMINE v. DI-PHENYL-BENZYL-AMINE.

u-DI-BENZYL-p-PHENYLENE-DIAMINE $C_6H_4(NH_2).N(CH_2.C_6H_5)_2$ [1:4]. *Amido-di-benzyl-aniline.* [90°]. Obtained by reduction of *p*-nitro-di-benzyl-aniline with tin and HCl. Glistening colourless needles. V. sol. ether and hot alcohol, sl. sol. cold alcohol. With Fe_2Cl_6 it gives a deep-red colouration, with Fe_2Cl_6 and H_2S a blue insoluble pp. By conc. HCl at 170° it is completely resolved into benzyl chloride and *p*-phenylene-diamine.

Benzaldehyde compound $C_6H_5.CH(OH).NH.C_6H_4.N(CH_2.C_6H_5)_2$. [130°]. Microcrystalline yellow pp. V. sol. benzene, sl. sol. ether, insol. alcohol (Matzudaira, *B.* 20, 1614).

BENZYL-PHOSPHINE C_7H_9P *i.e.* $C_6H_5.CH_2.PH_2$. (180°). From benzyl chloride, PH_4I, and ZnO (Hofmann, *B.* 5, 100). Oil, volatile with steam.—B′HI: decomposed by water into its components.

Benzyl-triethyl-phosphonium chloride $PEt_3(CH_2Ph)Cl$. From benzylidene chloride, tri-ethyl-phosphine and alcohol (Hofmann, *A. Suppl.* 1, 323).

Di-benzyl-phosphine $(CH_2Ph)_2PH$. [205°]. Prepared together with the preceding, and separated by steam-distillation, not being volatile. Groups of needles (from alcohol); insol. acids.

Tri-benzyl-phosphine $P(CH_2Ph)_3$. Appears to be formed as a by-product in the action of benzyl chloride on PNa_3 (Letts a. Collie, *Tr. E.* 30, 181). Splits up on distillation into phosphorus, *s*-di-phenyl-ethylene, dibenzyl, and toluene.

Tri-benzyl-phosphine oxide $(CH_2Ph)_3PO$. [213°]. Formed by heating PH_4I with benzylidene chloride at 130° and boiling the product with alcohol (Fleissner, *B.* 13, 1665). Formed also by the action of conc. $Ba(OH)_2$ on tetra-benzyl-phosphonium acid sulphate; a weak solution of baryta giving $P(C_7H_7)_4OH$ (Letts a. Collie, *Tr. E.* 30, 181). Needles; insol. water, sol. alcohol and ether. $(C_{21}H_{21}PO)_2HgCl_2$.—$(C_{21}H_{21}PO)_2Fe_2Cl_6$.—$(C_{21}H_{21}PO)_2CoCl_2$.—$(C_{21}H_{21}PO)_2PdCl_2$.—$(C_{21}H_{21}PO)_2PtCl_4$.—$(C_{21}H_{21}PO)_2ZnI_2$.—$(C_{21}H_{21}PO)_2Br_2$.—$(C_{21}H_{21}PO)_2S$.

Tri-benzyl-phosphine sulphide $(CH_2Ph)_3PS$. [206°]. Obtained by distilling the acid sulphate of tetra-benzyl-phosphonium (Letts a. Collie). Long thin needles, m. sol. alcohol.

Tetra-benzyl-phosphonium hydroxide $P(C_7H_7)_4OH$. [over 200°]. Obtained by adding $BaCO_3$ to the sulphate. Rhombohedral plates; v. sol. water and alcohol; alkaline to litmus. Decomposed by heat into $P(C_7H_7)_3O$ and toluene.

Tetra-benzyl-phosphonium salts.

Chloride $P(CH_2Ph)_4Cl$. [224°]. From benzyl chloride and PNa_3 (L. a. C.). Crystallises from water with 2aq, and from chloroform with $CHCl_3$. Split up by heat into tri-benzyl-phosphine, *s*-di-phenyl-ethylene, and HCl.

Platinochloride $\{P(CH_2Ph)_4Cl\}_2PtCl_4$.

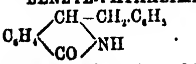
Sulphates. — $\{P(C_7H_7)_4\}_2SO_4$: [220°]. — $P(C_7H_7)_4SO_4H$: [217°].

Oxalate $P(C_7H_7)_4C_2O_4H$: needles.

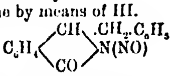
BENZYL-ISO-PHTHALIC ACID $C_{15}H_{12}O_4$ *i.e.* $C_6H_5.CH_2.C_6H_3(CO_2H)_2$. [243°]. From benzoyl-iso-phthalic acid by reduction with sodium-amalgam (Zincke, *B.* 9, 1765). Crystalline powder, v. sl. sol. water. -BaA″.—CaA″aq.

Benzyl-terephthalic acid
$C_6H_5.CH_2.C_6H_3(CO_2H)_2$. Obtained by reduction of benzoyl-terephthalic acid (Weber, *J.* 1878, 403). BaA″.

BENZYL-PHTHALIMIDINE $C_{15}H_{13}ON$ *i.e.*



[137°]. Colourless plates or scales. Formed by reduction of benzylidene-phthal-imidine by means of HI.

Nitrosamine 

[93°]; yellow crystals, easily soluble in benzene, ligroïn, and chloroform (Gabriel, *B.* 18, 1262).

BENZYL-PHTHALIMIDE
$C_6H_4:C_2O_2:N.CH_2.C_6H_5$. *Phthalyl-benzylamine.* [116°]. Long needles. Obtained by heating potassium phthalimide with benzyl chloride at 170°–180°. HCl at 200° splits it up into phthalic acid and benzylamine (Gabriel, *B.* 20, 2227).

BENZYL-PIPERIDINE $C_5H_{10}N(C_7H_7)$. (245°). Colourless liquid. Insol. water. Prepared by the action of benzyl chloride on piperidine.— $(B'HCl)_2PtCl_4$: sparingly soluble pp.

Methylo-iodide B'MeI. [145°]. Thick prisms. By moist Ag_2O it gives an alkaline hydrate which on dry-distillation yields methyl-benzyl-piperidine (Schotten, *B.* 15, 423).

BENZYL PROPIONATE $C_{10}H_{12}O_2$ *i.e.* $C_6H_5.CH_2.O.CO.CH_2.CH_3$. (220°). S.G. $\frac{16.5}{17.5}$ 1·0360. Decomposed by Na into sodium propionate and benzyl phenyl-butyrate (Conrad a. Hodgkinson, *A.* 193, 320).

v-**BENZYL-PYRROL** $C_4H_4:N.C_7H_7$. (247° uncorr.). Colourless crystalline solid. Melts when touched with the hand. V. sol. alcohol and ether, nearly insol. water (Ciamician a. Silber, *B.* 20, 1369).

v **BENZYL-PYRRYLENE-DI-METHYL-DI-KETONE** $C_4H_2(CO.CH_3)_2NC_7H_7$. *v-Benzyl-di-acetyl-pyrrol.* [130°]. Formed by heating *v*-benzyl pyrrol with Ac_2O at 210°. Colourless plates. Sol. ether and benzene, sl. sol. water, nearly insol. petroleum-ether (Ciamician a. Silber, *B.* 20, 1370).

BENZYL-QUINOLINIUM HYDROXIDE *v.* *Benzylo-hydroxide* of QUINOLINE.

BENZYL-ROSANILINES. From rosaniline and benzyl chloride (Dahl, *D. P. J.* 263, 393); *v.* ROSANILINE.

Methylo-iodide. From rosaniline, MeI and MeOH (Hofmann, *B.* 6, 263).

BENZYL SELENIDE $(C_6H_5.CH_2)_2Se$. [46°]. From benzyl chloride and P_2Se_5 (C. L. Jackson, *A.* 179, 1). Long needles or prisms (from alcohol); faint odour, insol. water, v. sol. alcohol and ether. HNO_3 forms 'selenobenzyl nitrate' [88°]. - $\{(C_7H_7)_2Se\}_2PtCl_4$.

Benzyl diselenide $(CH_2Ph)_2Se_2$. [90°]. Formed by boiling Na_2Se_2, benzyl chloride, and alcohol for some hours (J.). Unctuous yellow scales (from alcohol). With MeI it forms $(CH_2Ph)SMe_2I$, [65°] from which may be obtained $\{(CH_2Ph)SMe_2Cl\}_2PtCl_4$. Conc. HNO_3 forms toluene-exo-selinic acid, $C_6H_5.CH_2.SeO_2H$.

BENZYL SELENO-CYANIDE C_8H_7NSe *i.e.* $C_6H_5.CH_2.SeCy$. [72°]. From benzyl chloride and potassium selenocyanide (Jackson, *B.* 8, 321). Prismatic needles with repulsive odour; insol. water, v. sol. hot alcohol. HNO_3 forms $C_6H_4(NO_2).CH_2.SeCy$ [123°].

BENZYL-SELEN-UREA $C_8H_{10}N_2Se$ *i.e.* $NH_2.CSe.NH.CH_2Ph$. [70°]. From benzylamine hydrochloride and alcoholic potassium selenocyanide (Spica, *G.* 7, 90). Sol. water, alcohol, and ether, gradually depositing Se. Conc. HCl forms benzylamine, Se, and HCN.

u-**di-benzyl-seleno-urea** $NH_2.CSe.N(CH_2Ph)_2$. [150°]. From dibenzylamine hydrochloride and KSeCy. Thin prisms or needles; v. sol. hot water, alcohol, and ether. Conc. HCl forms Se, CNH, and dibenzylamine.

TETRA-BENZYL-SILICANE $C_{28}H_{28}Si$ *i.e.* $Si(CH_2Ph)_4$. *Silicon-tetra-benzyl.* [128°]. (above 550°). S.G. $\frac{22}{}$ 1·078. Formed by the action of sodium upon a mixture of benzyl chloride and $SiCl_4$, with addition of a little acetic ether (Polis, *B.* 18, 1543; 19, 1023). Large mono-symmetrical prisms, sol. ether, benzene, and chloroform, sl. sol. alcohol. May be distilled.

BENZYL SULPHIDE $C_{14}H_{14}S$ *i.e.* $(CH_2Ph)_2S$. [50°]. From benzyl chloride and alcoholic K_2S (Märcker, *A.* 136, 88). Thick trimetric tablets (from ether), $a:b:c$ = ·813:1:·515 (Forst, *A.* 178, 370; Bodewig). On distillation it gives *s*-di-phenyl-ethylene and its sulphide (Barbier, *C. R.* 78, 1772), toluene, benzyl mercaptan, *s*-di-phenyl-acetylene sulphide SC_2Ph_2, and thionessal $C_{28}H_{18}S$. MeI forms SMe_3I, benzyl iodide and $(CH_2Ph)SMe_2I$; the latter gives rise to the compound $\{(CH_2Ph)SMe_2Cl\}_2PtCl_4$. Ethyl iodide at 100° forms similarly $(C_7H_7)SEt_2I$ whence $\{(C_7H_7)SEt_2Cl\}_2PtCl_4$ (Schöller, *B.* 7, 1274; *cf.* Cahours, *A. Ch.* [5] 10, 21).

DI-BENZYL DI-SULPHIDE $(C_6H_5.CH_2)_2S_2$. *Sulphobenzol.* [70°].

Formation.—1. By the action of an alcoholic solution of KHS or K_2S on benzylidene dichloride.—2. By the action of alcoholic KHS on (α)-thiobenzoic aldehyde (Klinger, *B.* 15, 861).— 3. By the oxidation of benzyl mercaptan by air or bromine (Märcker, *A.* 140, 86).—4. By the action of K_2S_2 on benzyl chloride in alcohol (M.).

Properties.—White plates. Gives a crystalline pp. $(C_{14}H_{14}S_2AgNO_3)$ with an alcoholic solution of $AgNO_3$.

BENZYL-SULPHINIC ACID *v.* TOLUENE EXO-SULPHINIC ACID.

BENZYL SULPHOCYANIDE
$C_6H_5.CH_2.S.CN$. [41°] (B.); [38°] (H.); (c. 233°) (B.); (256°) (H.). From benzyl chloride and alcoholic potassium sulphocyanide (Henry, *B.* 2, 636; Barbaglia, *B.* 5, 689). Prisms (from alcohol), insol. water; pungent smell. Combines with HBr, forming a compound decomposed by water. Fuming nitric acid forms $C_6H_4(NO_2).CH_2.S.Cy$.

DI-BENZYL-SULPHONE $C_{14}H_{14}SO_2$ *i.e.* $(CH_2Ph)_2SO_2$. [150°].

Formation.—1. Together with $C_6H_5.CH_2.SO_3K$ by the action of K_2SO_3 on benzyl chloride (Vogt a. Henninger, *A.* 165, 375).—2. By oxida-

tion of di-benzyl sulphoxide with $KMnO_4$ and HOAc (Otto a. Lüders, *B.* 13, 1284).—3. By the action of benzyl chloride on sodium benzene-sulphinate.—4. By oxidation of di-benzyl sulphide.

Properties.—Small needles. Insol. water, sol. alcohol, benzene, and acetic acid. By oxidising agents it is readily oxidised to benzoic and sulphuric acids (Otto, *B.* 13, 1277).

BENZYL-SULPHONIC ACID *v.* TOLUENE-*exo*-SULPHONIC ACID.

DIBENZYL - SULPHONIC ACID *v.* DI-PHENYL-ETHANE SULPHONIC ACID.

DI-BENZYL SULPHOXIDE $C_{14}H_{14}SO$ *i.e.* $(CH_2Ph)_2SO$. [133°]. From di-benzyl sulphide and cold HNO_3 (S.G. 1·3) (Märcker, *A.* 136, 89; Otto a. Ludwig, *B.* 13, 1284). Laminæ (from water or alcohol).

BENZYL-SULPHUROUS ACID *v.* TOLUENE SULPHONIC ACID.

BENZYL-TARTRONIC ACID $C_{10}H_{10}O_5$ *i.e.* $C_6H_5.CH_2.C(OH):(CO_2H)_2$. [143°]. Formed simultaneously with cinnamic acid by the action of KOH on benzyl-chloro-malonic ether. On heating it forms β-phenyl-α-oxy-propionic acid (phenyl-lactic acid [98°]) (Conrad, *B.* 13, 2160; *A.* 209, 245).

BENZYL-TEREPHTHALIC ACID *v.* BENZYL-PHTHALIC ACID.

BENZYL - THIO - CARBAMIDINE $C_8H_{10}N_2S$ *i.e.* $NH:C(NH_2).S.CH_2Ph$. *Cyanamide benzyl-mercaptan.* [72°]. From benzyl chloride and thio-urea (Bernthsen a. Klinger, *B.* 12, 575). Slender needles, m. sol. water; decomposed by heat into benzyl mercaptan and di-cyan-di-amide.—B'HCl. [168°].—$B'_2H_2PtCl_6$.

BENZYL - THIO - CARBIMIDE $C_6H_5.CH_2.N:CS$. *Benzyl mustard oil.* (243°). Benzylamine is dissolved in CS_2 and the product boiled with alcohol and $HgCl_2$ (Hofmann, *Z.* [2] 4, 690; *B.* 1, 201). Oil, smelling like water-cress.

BENZYL-THIO-GLYCOLLIC ACID *v.* THIO-GLYCOLLIC ACID.

BENZYL-THIO-UREA $C_8H_{10}N_2S$ *i.e.* $(CH_2Ph)NH.CS.NH_2$. [101°]. From potassium sulphocyanide and benzylamine hydrochloride (Paterno a. Spica, *G.* 5, 388; *B.* 9, 81). Sol. water and alcohol.

Benzoyl derivative $C_7H_7NH.CS.NHBz$. [145°]. From benzoyl sulphocyanide and benzylamine (Miquel, *A. Ch.* [5] 11, 313).

s-**Di - benzyl - thio - urea** $(Ph.CH_2.NH)_2CS$. [114°]. From alcoholic benzylamine and CS_2 (Strakosch, *B.* 5, 692). Four-sided plates, insol. water, sol. alcohol and ether. Converted by HgO into di-benzyl-urea. Alkyl iodides give the following derivatives:

$PhCH_2.NH.CS.NMe.CH_2Ph$.—
$(C_7H_7.NH.CS.NMeC_7H_7)_2H_2PtCl_6$.—
$C_7H_7NH.CS.NMeC_7H_7HI$ [99°].—
$PhCH_2.NH.CS.NEt.CH_2Ph$.—
$(C_7H_7NH.CS.NEtC_7H_7)_2H_2PtCl_6$.—
$C_7H_7NH.CS.NEtC_7H_7HI$ [93°].—
$C_7H_7NH.CS.NEtC_7H_7H_2SO_4$.—
$PhCH_2 NH.CS.NPr.CH_2Ph$.—

$PhCH_2.NH.CS.N(C_5H_{11}).CH_2Ph$ (Reimarus, *B.* 19, 2348).

u-**Di - benzyl - thio - urea** $(PhCH_2)_2N.CS.NH_2$. [157°]. From potassium sulphocyanide and dibenzylamine hydrochloride (P. a. S.). Large needles, m. sol. water.

BENZYL-THYMOL $C_{17}H_{20}O$ *i.e.* $C_6H_2MePr(CH_2Ph)(OH)$. (255°) at 8 mm. Formed, together with di-benzyl-thymol by heating benzyl chloride with thymol and zinc-dust (Mazzara, *G.* 11, 346). Oil, insol. aqueous alkalis, sol. alcohol and ether. Fe_2Cl_6 gives a red colour on heating.

Acetyl derivative $C_{17}H_{19}AcO$. (245°) at 8 mm.

Di-benzyl thymol $C_{24}H_{26}O$ *i.e.* $C_6HMePr(CH_2Ph)_2OH$. [76°]. Prepared as above. Silky laminæ, sol. ether and HOAc, insol. water and aqueous alkalis. Fe_2Cl_6 gives a red colour on heating.

Acetyl derivative $C_{24}H_{25}AcO$. [c. 84°].
Methyl derivative $C_{24}H_{25}MeO$. [90°].
Benzoyl derivative $C_{24}H_{25}BzO$. [c. 78°].

BENZYL - TOLUENE *v.* PHENYL - TOLYL-METHANE.

DI-BENZYL-TOLUENE $C_{21}H_{20}$ *i.e.* $CH_3.C_6H_3(CH_2Ph)_2$. (c. 394°). A product of the action of benzyl chloride on toluene in presence of zinc-dust (Weber a. Zincke, *B.* 7, 1154).

BENZYL-*p*-TOLUIDINE $PhCH_2.NH.C_6H_4Me$. (313°). From benzylidene-*p*-toluidine (Kohler, *A.* 241, 359).

Di-benzyl-*p*-toluidine $C_{21}H_{21}N$ *i.e.* $(Ph.CH_2)_2N.C_6H_4Me$. [55°]. From benzyl chloride and *p*-toluidine (Cannizzaro, *A. Suppl.* 4, 80). Slender needles, m. sol. cold alcohol. Weak base.

BENZYL-TOLYL- *v.* TOLYL-BENZYL-.

BENZYL - TOLYL - METHANE *v.* PHENYL-TOLYL-ETHANE.

BENZYL-TOLYL OXIDE *v.* BENZYL ALCOHOL.

BENZYL-UREA $C_8H_{10}N_2O$ *i.e.* $NH_2.CO.NH.CH_2Ph$. [147°]. Formed, together with di-benzyl-urea, by heating benzyl chloride with potassium cyanate in alcoholic solution (Cannizzaro, *G.* 2, 41). Also from benzyl cyanate and alcoholic NH_3 (Letts, *C. J.* 25, 448) or from benzylamine chloride and potassium cyanate (Paterno a. Spica, *G.* 5, 388; *B.* 9, 81). Long needles (from alcohol); m. sol. water. At 200° it splits up into NH_3 and *s*-di-benzyl-urea.

s-**Di-benzyl-urea** $(CH_2Ph.NH)_2CO$. [167°].

Formation.—1. From benzyl chloride and KNCO or urea.—2. From benzyl-urea by heating.—3. By heating benzyl alcohol with urea nitrate (Campisi a. Amato, *G.* 1, 39; *B.* 4, 412).—4. From *s*-di-benzyl-thio-urea, HgO, and alcohol (Strakosch, *B.* 5, 692).

Properties.—Needles, insol. water, v. sol. alcohol. Weak base.

u-**Di-benzyl-urea** $(CH_2Ph)_2N.CO.NH_2$. [125°]. From di-benzyl-amine hydrochloride and KNCO (Paterno a. Spica, *G.* 5, 388; *B.* 9, 81). Thick prisms; sl. sol. cold water.

BENZYL-URETHANE *v.* BENZYL-CARBAMIC ACID.

BENZYL-*m*-XYLENE $C_{15}H_{16}$ *i.e.* $C_6H_5.CH_2.C_6H_3Me_2$. *Phenyl - xylyl - methane* (296° i. V.). From *m*-xylene, benzyl chloride, and zinc-dust or Cu (Zincke, *B.* 5, 799; 9, 1761). Oxidation gives benzoyl-iso-phthalic acid. Appears also to be formed by reducing phenyl xylyl ketone with HI (Söllscher, *B.* 15, 1682).

Benzyl-*p*-xylene. (295°). From *p*-xylene, benzyl chloride and zinc-dust (Z.).

BENZYL XYLYL KETONE
$C_6H_5.CH_2.CO.C_6H_3(CH_3)_2$. [1:2:4]. *Dimethyl-*

deoxybenzoin (above 350°). Fluid. Formed by the action of Al_2Cl_6 on a mixture of *m*-xylene and phenyl-acetyl-chloride. On oxidation it gives di-methyl-benzoic acid (Söllscher, *B.* 15, 1681).

BERBAMINE $C_{18}H_{19}O_3N$. [156°]. Occurs in the root of *Berberis vulgaris*, together with berberine, oxy-acanthine, and at least one other alkaloid. Small plates, containing 2aq. Easily sol. ether. The hydrochloride forms small plates, the nitrate needles.—$B'_2H_2Cl_2PtCl_4$ 5 or 6aq: yellow crystalline pp., sl. sol. cold water (Hesse, *B.* 19, 3193).

BERBERIC ACID $C_8H_8O_4$aq. An acid formed by fusing berberine with KOH (Hlasiwetz a. Gilm, *J.* 1864, 407). Needles; v. sol. alcohol and ether, m. sol. water. Fe_2Cl_6 gives a green colour turned red by ammonium tartrate. Reduces hot Fehling's solution and silver solution.

BERBERINE $C_{20}H_{17}NO_4 4\frac{1}{2}$aq. [120°]. S. 22 at 21°. S. (alcohol) 1 at 15°. Occurs in the root of the barberry, *Berberis vulgaris*, together with oxy-acanthine (*q. v.*), berbamine and another alkaloid (Buchner, *A.* 24, 228; Hesse, *B.* 19, 3190). Occurs also in Colombo-root (*Cocculus palmatus*) (Fleitmann, *A.* 59, 160; Bödeker, *A.* 66, 384; 69, 40); in *Menispermum fenestratum* (Perrins, *C. J.* 15, 339); in Abeocouta bark from *Cœlocline polycarpa* (Stenhouse, *Ph.* 14, 455; *C. J.* 20, 187; Daniel, *A.* 105, 360); in *Leontice thalictroïdes* (Mayer, *J. Ph.* [3], 46, 496); in *Xanthoxylon clava Herculis* (Chevallier a. Pelletan, *Berz. J.* 7, 266; Perrins, *A. Suppl.* 2, 171); in bark of *Geoffroyea inermis* (Gastell, *J.* 1866, 480); in *Coptis trifolia* (Gross, *J.* 1874, 914); and in the root of *Evodia glauca* (Martin, *Ph.* [3] 13, 337).

Preparation.—1. The finely powdered root of *Hydrastis canadensis* is extracted with alcohol; H_2SO_4 is added to the cooled extract, and the pp. decomposed by NH_3. The operation is repeated a second time (Lloyd, *Ph.* [3] 10, 125; *cf.* Merril, *Am. J. Pharm.* 35, 97; Procter, *C. N.* 9, 112). 2. Barberry root is exhausted with boiling water; the extract evaporated, and treated with 92 p.c. alcohol. The berberine is purified by crystallisation from water or alcohol (Buchner).

Properties.—Silky yellow needles; tastes bitter; sl. sol. cold water and alcohol, insol. ether. Turned brown by ammonia. On adding iodine in potassium iodide to a solution of berberine hydrochloride the periodide is ppd. It crystallises from alcohol in red needles, but on adding water, green plates separate.

Reactions.—1. *Zinc* and *dilute acids* form hydro-berberine. 2. *Potash-fusion* produces two acids, $C_8H_8O_4$, and $C_9H_8O_5$ (Hlasiwetz a. Gilm, *J.* 1864, 406). 3. *Nitric acid* oxidises it to berberonic acid.—4. $KMnO_4$ in presence of KHO forms hemipic acid, [162°] (E. Schmidt a. Schilbach, *Ar. Ph.* [3] 25, 164).

Salts.—(Fleitmann, *A.* 59, 160; Henry, *A.* 115, 132; Perrins, *C. J.* 15, 339; Hlasiwetz, *A. Suppl.* 2, 191). — B'HCl: slender yellow needles. — B'HCl 4aq. — B'HCl 2aq. S.G. $\frac{19.4}{4}$ 1·397 (Clarke, *Am.* 2, 175). — $B'_2H_2HgCl_4$. —$B'HHgCl_3$ (Hinterberger, *A.* 82, 314).— $B'_2H_2Cl_2HgCy_2$ (Kohl a. Swoboda, *J.* 1852, 550). —$B'_2H_2PtCl_6$: small needles. S.G. $\frac{19}{4}$ 1·758 (C.). —$B'HAuCl_4$: maroon-coloured needles.— B'HBr $1\frac{1}{2}$aq. — B'HI. — B'HI. — B'HCN. — B'HSCN $1\frac{1}{2}$aq. — $B'_4H_4FeCy_6$. — $B'_3H_3FeCy_6$. —$B'H_2C_2O_4$. — $B'HClO_3$. — $B'C_4H_6O_4\frac{1}{2}$aq.— $B'C_4H_6O_6\frac{1}{2}$aq.—$B'C_4H_5(SbO)O_6$ (Stenhouse, *Pr.* 12, 491). — $B'_2H_2Cr_2O_7$. — $B'C_6H_2(NO_2)_3OH$.— $B'H_2SO_4$.—$B'HNO_3$.—$B'_2H_2S_2O_3Ag_2S_2O_3$.

Methylo-iodide B'MeI: needles (Bernheimer, *G.* 13, 315).

Ethylo-iodide B'EtI: needles.

Hydroberberine $C_{20}H_{21}NO_4$. Obtained by reducing berberine in acid solution with zinc (Hlasiwetz a. Gilm, *A. Suppl.* 2, 191). Granules or needles (from alcohol). Reconverted into berberine by HNO_3.

Salts.—B'HCl. — $B'_2H_2PtCl_6$. — $B'_2H_2SO_4$. —$B'H_2SO_4$. — $B'_4(H_2SO_4)_3 4$aq (?). — B'HI.— $B'HNO_3$.

Methylo-iodide B'MeI: trimetric crystals, $a:b:c = 1·033:1:1·789$. —B'MeOH (Bernheimer, *G.* 13, 342).

Ethylo-iodide B'EtI: prisms.

BERBERONIC ACID *v.* Pyridine-tri-carboxylic acid.

BERGAMOT, OIL OF. An aromatic essential oil expressed from the rind of an orange, *Citrus bergamia*. Its S.G. is ·87. It contains a stearoptene, a terpene, and a terpene hydrate (?). By rectification a liquid (183°) may be got, which absorbs HCl (Soubeiran a. Capitaine, *J. Ph.* 26, 68, 509). The stearoptene (*Bergaptene*) is deposited after long keeping. It is solid, [206°], but volatilises without decomposition. It may be $(C_3H_2O)x$ (Mulder, *A.* 31, 70; Ohme, *A.* 31, 316).

BERGENITE $C_6H_{10}O_5$ aq. [130°]. S.G. 1·5 $[\alpha]_D = -51°\ 36'$. Obtained from Siberian saxifrage (*Bergenia siberica*) by extracting with hot water, ppg. the tannins with lead acetate, and evaporating to crystallisation (Morelli, *C. R.* 93, 646). Trimetric prisms. Tastes bitter. V. sl. sol. cold alcohol and water.

Acetyl derivative $C_6H_9AcO_5$: amorphous, v. sol. water, alcohol, and ether.

Tri-acetyl derivative $C_6H_7Ac_3O_5$.

Penta-acetyl derivative $C_6H_5Ac_5O_5$.

BERLIN BLUE = Prussian Blue *v.* *Ferrocyanide of iron* under Cyanides.

BERONIC ACID *v.* Pyridine di-carboxylic acid.

BERYLLIUM. Be. (*Glucinum.*) At. w. 9·08. Mol. w. unknown. S.G. $\frac{20°}{20}$ (after compression) 1·85 (Humpidge, *Pr.* 39, 1). S.H. (100°) ·4702; (200°) ·540; (400°) ·6172; (500°) ·6206 (Humpidge, *Pr.* 39, 1). S.H. (20°) ·397; (73°) ·448; (157°) ·519; (257°) ·581 (Meyer's calculation, *B.* 13, 1780, from data of Nilson and Pettersson who worked with metal containing about 95 p.c. Be; *B.* 13, 1451). S.V.S. 4·92. Crystallises in hexagonal, holohedral, forms; $a:c = 1:1·5801$ (Brögger a. Flink, *B.* 17, 849).

Occurrence.—Only in combination; in *beryl* $(3BeO.Al_2O_3.6SiO_2)$ and some other silicates, also in *chrysoberyl* $Al_2O_3.BeO$. Beryllium oxide was recognised as a distinct body in 1797 by Vauquelin, the metal was obtained by Wöhler in 1827, but approximately pure beryllium was not prepared until 1885, in which year Humpidge obtained specimens containing 99·2 p.c. Be, ·1 Fe, and ·7 BeO.

Preparation.—Wöhler (*P.* 13, 577) obtained an impure metal by the action of K on fused

$BeCl_2$: Debray (*C. R.* 88, 784) obtained purer specimens by using Na and a special form of apparatus. Nilson a. Pettersson, by decomposing $BeCl_2$ by Na in closed iron crucibles heated in a wind-furnace (*B.* 11, 381), and sifting the crystals through Pt gauze (*B.* 13, 1455), obtained specimens containing 94·4 p.c. Be (BeO = 4·89, Fe = ·70). Humpidge (*Pr.* 38, 188; 39, 1) purified BeO by solution in $(NH_4)_2CO_3Aq$ and decomposing the solution by steam; he mixed the BeO thus obtained with pure charcoal and starch paste and heated in Cl in a glazed porcelain tube; the $BeCl_2$ thus obtained was placed in an iron boat, and this in an iron tube surrounded by another tube of hard glass; another iron boat contained Na; the Na was heated in a stream of H, and the $BeCl_2$ was then vaporised (in H) over the molten Na. The crystals of Be were washed in dilute NaOHAq, to remove BeO, then in water, and dried.

Properties.—Steel-coloured, hard, hexagonal, holohedral (Brögger a. Flink, *B.* 17, 849) crystals. Unchanged in ordinary air; scarcely changed by heating in air. Scarcely acted on by O or S at red heat, but burns in Cl to $BeCl_2$ (Nilson a. Pettersson, *B.* 11, 381). Burns in O-H flame (Humpidge, *T.* 174, 601). Dissolves slowly in acids, also in aqueous alkalis, with evolution of H. Many of the properties ascribed to Be by Wöhler (*P.* 13, 577), and Debray (*A. Ch.* [3] 44, 5), were the results of experiments with very impure material. Emission-spectrum characterised by the lines 3320·5, 2649·4, 2493·2, and 2477·7, of which 3320·5 is the most prominent (Hartley, *C. J.* 43, 316). The atomic weight of Be has been determined (i) by analyses, and determinations of V.D., of $BeCl_2$ and $BeBr_2$; (ii) by determinations of S.H. of Be; (iii) by analyses of various compounds, especially recently of the pure crystallised sulphate by Nilson a. Pettersson (*B.* 13, 1451) [for older analyses *v.* Berzelius, *P.* 8, 187; Awdejew, *P.* 56, 101; Klatzo, *J. pr.* 106, 227]; (iv) by the application of the periodic law. There has been much investigation and discussion concerning the value to be given to the atomic weight of Be; some chemists insisted that 13·65 is the true value, and that the oxide is Be_2O_3. The determinations of the V.D. of $BeCl_2$ and $BeBr_2$, the careful measurement of the S.H. of almost pure Be, and the consideration of the physical and chemical relations of Be and its compounds to other elements carried out on the lines suggested by the periodic law, have finally established the value 9·08–9·1 for the atomic weight of Be. The S.H. of Be increases rather rapidly as the temperature increases, and approaches a constant value, equal to about ·62, between 400° and 500° (Humpidge, *Pr.* 39, 1). The relation between S.H. and temperature is expressed by the empirical formula $K_t = \cdot 3756 + \cdot 00106t - \cdot 000001 14t^2$ (Humpidge, *Pr.* 38, 188). The product of S.H. into At. w. ($\cdot 62 \times 9\cdot 1 = 5\cdot 64$) is lower than the mean value of this quantity for the solid elements, but is nearly the same as that obtained for B, C, and Si. The atom of Be is divalent in the gaseous molecules $BeCl_2$ and $BeBr_2$; these are the only compounds of Be at present known in the gaseous state. A comparison of the spectrum of Be with those of In and Al on the one hand, and of Mg, Ca, Ba, Sr, on the other, shows that Be is rather to be classed with the latter than with the former elements; the value 9·1 for the atomic weight of Be is thus confirmed (*v.* Hartley, *C. N.* 48, 195). Beryllium is a markedly positive, or metallic, element; it does not exhibit allotropy. It is chemically related to Mg, Ca, Sr, and Ba, in much the same way that Li is related to Na, K, Cs, and Rb. BeO resembles MgO, but is distinctly less basic; *e.g.* it dissolves in KOHAq, and does not combine directly with H_2O; compare also $[BeO^2H^2, H^2SO^4Aq] = 16,096$, with $[MgO^2H^2, H^2SO^4Aq] = 31,216$. Analogies also exist between Be and Al; *e.g.* the existence of many basic salts; Be, however, does not form an alum; $BeCl_2$ does not combine with NaCl and KCl as Al_2Cl_6 does. In dilute acid solutions Be is electronegative to Mg but positive to Al; in caustic alkali solutions the electrochemical order is +Al, Mg, Be− (Humpidge, *Tr.* 174, 601). Be forms only one series of compounds, $BeCl_2$, $BeSO_4$, $Be2NO_3$, &c.; it exhibits a marked tendency to form basic salts, *e.g.*, $BeSO_4.BeO.3H_2O$, $BeCO_3.3BeO.5H_2O$, &c. Brauner (*B.* 14, 53) sums up the chemical relations of Be in the three statements (1) Li:Be = Be:B. (2) Li:Na = Be:Mg = B:Al. (3) Li:Mg = Be:Al = B:Si. The chemical relations of Be will be more fully discussed in the art. MAGNESIUM METALS; *v.* also the remarks on Group II. in art. CLASSIFICATION. The following are the principal papers bearing on the At. w. of Be: Reynolds, *P. M.* [5] 3, 38; *ibid. Pr.* 35, 218; Humpidge, *Pr.* 35, 358; 38, 188; 39, 1; Hartley, *C. J.* 43, 316; *ibid. Pr.* 36, 462; Carnelley, *Pr.* 29, 190; *ibid. B.* 17, 1357; Brauner, *B.* 11, 872; 14, 53; Meyer, *B.* 11, 577; 13, 1780; Nilson a. Pettersson, *B.* 11, 381, 906; 13, 1451, 2035; 17, 987.

Reactions.—As most of the reactions said to characterise Be have been obtained by experimenting with material far from pure, the following statements must be accepted as provisional only.—1. *Hydrochloric acid*, whether gaseous or aqueous, reacts readily to produce $BeCl_2$.—2. *Sulphuric acid* dissolves Be, forming $BeSO_4Aq$.—3. *Nitric acid* acts very slowly even when hot and concentrated.—4. Be dissolves in warm KOHAq or NaOHAq.

Combinations.—1. Be combines readily with Cl, Br, and I to form $BeCl_2$, $BeBr_2$, and BeI_2 respectively.—2. It also combines very readily with Si; and, according to the observations of Wöhler, made, however, with very impure material, with P, Se, and S; later experiments seem to show that Be and S do not combine when heated together (Nilson a. Pettersson, *B.* 11, 381).—3. An *alloy* of Be and Fe was described by Stromeyer as a white solid, less malleable than iron, obtained by strongly heating BeO with Fe and charcoal.

Detection.—1. *Caustic potash or soda* pps. $BeO.H_2O$ soluble in excess, but reppd. on diluting and boiling.—2. *Ammonium carbonate* pps. the carbonate easily soluble in excess; this reaction distinguishes salts of Be from salts of Al.—3. Be salts give no colour when heated with $Co.2NO_3$.

Estimation.—As oxide, by ppg. by excess of NH_3Aq, washing, drying, and strongly heating. BeO is separated from Al_2O_3 by the action of

$(NH_4)_2CO_3$ (*v.* Hofmeister, *J. pr.* 76, 1); or by converting the alumina into potash alum (*v.* Scheffer, *A.* 109, 144).

Beryllium, Alloys of. Little or nothing is known; *v.* BERYLLIUM, *Combinations*, No. 3.

Beryllium, Bromide of. $BeBr_2$. Mol. w. 168·6. [abt. 600°] (Carnelley, *B.* 17, 1357); sublimes readily at 450°. V. D. 90 (Humpidge, *Pr.* 38, 188).

Preparation.—1. By heating Be in Br vapour (Wöhler, *P.* 13, 577).—2. By heating BeO mixed with charcoal and made into a paste with starch, in dry Br (Humpidge, *T.* 174, 601). Crystals of hydrated $BeBr_2$ are obtained by dissolving freshly ppd. $BeO.H_2O$ in HBrAq, and evaporating (Berthemot, *A. Ch.* [2] 44, 394).

Properties. Long white needles; very deliquescent. Heated in air, partly sublimes, and is partly decomposed into BeO and Br.

Beryllium, Chloride of. $BeCl_2$. Mol. w. 80, at low temps. 160 = Be_2Cl_4. [about 600°] but sublimes considerably lower (Carnelley, *C. J.* 37, 26; *v.* also *ibid. B.* 17, 1357). V. D. (685° to 1500°) 40·96 (mean of 4); V. D. (520°) 60·4 (Nilson a. Pettersson, *B.* 17, 987; *J. pr.* [2] 33, 1).

Preparation.—1. By heating Be in Cl.—2. By heating BeO and C in Cl, and subliming in HCl.—3. By heating Be in perfectly dry HCl, and subliming in the same (Nilson a. Pettersson, *B.* 17, 987).

Properties.—Snow-white crystalline mass; easily fused and volatilised; melts to a colourless refractive liquid; may be sublimed unchanged in pure dry N or CO_2; but is easily decomposed into BeO and Cl if a little air is present (Nilson a. Pettersson, *B.* 17, 987). Is practically a non-conductor of electricity (Nilson a. Pettersson, *B.* 11, 382; Humpidge, *T.* 174, 601).

Reactions.—Dissolves in water with production of much heat; on evaporation, an *oxychloride* $Be_2OCl_2.H_2O$ (= $BeCl_2.BeO.H_2O$) is obtained; if the solution is placed over H_2SO_4 under a bell-jar, crystals of $BeCl_2.4H_2O$ separate out (Awdejew, *P.* 56, 101; Atterberg, *Bl.* [2] 21, 358).

Combinations.—1. With *chlorides of various heavy metals*, to form double compounds; especially $BeCl_2.3HgCl_2.6H_2O$, and $BeCl_2.SnCl_4.8H_2O$ (Atterberg, *B.* 7, 473); $BeCl_2.PtCl_4.9H_2O$ (Thomsen, *B.* 3, 827; 7, 75). The salt $BeCl_2.PtCl_4.9H_2O$ is analogous in composition to the Ca double salt $CaCl_2.PtCl_4.9H_2O$; dried from 120° to 200° the Be salt retains $4H_2O$, and corresponds with double Ba-Pt salt, $BaCl_2.PtCl_4.4H_2O$. 2. With *ether* to form $BeCl_2.2(C_2H_5)_2O$ (Atterberg, *Bl.* [2] 21, 358).

Beryllium, Fluoride of. Hydrated BeO dissolves easily in HFAq; on evaporation, a transparent, gum-like, mass is obtained which becomes opaque at 100°, but remains soluble in water; this is probably BeF_2 (Berzelius). The double compounds $BeF_2.2KF$, and $BeF_2.KF$, are described by Marignac (*A. Ch.* [4] 30, 45), the former obtained by adding much KFAq, the latter by adding little KFAq, to a solution of $BeO.H_2O$ in HFAq, and evaporating. The compounds $2NaF.BeF_2$, $NaF.BeF_2$, and $2NH_4F.BeF_2$ are also described by Berzelius.

Beryllium, Hydrated oxide of, *v.* BERYLLIUM, HYDROXIDES OF.

Beryllium, Hydroxides of. A compound of Be, H, and O, agreeing in composition with the formula BeO_2H_2 (= $BeO.H_2O$) is obtained as a white powder by ppg. a hot solution of a Be salt by NH_3Aq, or KOHAq, boiling, collecting, washing, and drying at 100° (Atterberg, *Bl.* [2] 21, 358; Weeren, *P.* 92, 91); on heating more highly, BeO remains. Van Bemmelen (*J. pr.* [2] 26, 227) says that the pp. by KOHAq has the composition $BeO.H_2O$ only when heated to 150°–180°: he describes a gelatinous hydrate, $BeO.H_2O$, obtained by the action of NH_3Aq on $BeSO_4$Aq, washing with cold water and drying in dry air at 15°–20°; the composition of this hydrate is constant up to 200°. The compound BeO_2H_2 is not re-formed by the action of water on BeO (for more details of this action *v.* Van Bemmelen, *l.c.*); it seems better to regard it as a hydrated oxide, $BeO.H_2O$, than as a hydroxide $Be(OH)_2$. Other hydrates of BeO are said to be obtained by drying the pp. by NH_3Aq over H_2SO_4, or merely in air, but the composition of these bodies is variable (*v.* Schaffgotsch, *P.* 50, 183; Atterberg, *B.* 7, 473; Van Bemmelen, *J. pr.* [2] 26, 227). The gelatinous $BeO.H_2O$ is easily soluble in acids, also in NaOHAq and KOHAq, and in $(NH_4)_2CO_3$Aq. By boiling the solution in KOHAq a ppt. of $3BeO.4H_2O$ (Atterberg, *B.* 7, 473) is obtained (but *v.* Van Bemmelen, *J. pr.* [2] 26, 227). BeO_2H_2 acts as a basic hydroxide towards acids; Thomsen gives the following values for its heats of neutralisation, solid BeO_2H_2 being used in each case (*Th.* 1, 363); $[BeO^2H^2, H^2SO^4Aq] = 16{,}096$; $[BeO^2H^2, 2HClAq] = 13{,}644$. These values are much less than those for the alkaline earth hydroxides (about 31,000 for H_2SO_4Aq).

Beryllium, Iodide of. BeI_2. Mol. w. unknown, as V.D. has not been determined. Described as colourless needles obtained by heating together Be and I (Wöhler, *P.* 13, 577; Debray, *A. Ch.* [3] 44, 5). Easily decomposed by action of hot air into BeO and I (Debray, *l.c.*).

Beryllium, Oxide of. BeO. Mol. w. unknown. S.G. 3·016. S.H. (0° to 100°) ·2471 (Nilson a. Pettersson, *B.* 13, 1454). S.V.S. 8·3.

Preparation.—Beryl is fused with $NaKCO_3$ in graphite crucibles in a wind-furnace; the fused mass is heated for some time with excess of H_2SO_4Aq, water is added and SiO_2 removed by filtration, the liquid is evaporated until a crust begins to form and is then allowed to stand for 24 hours or more; potash alum and K_2SO_4 separate out; the mother liquor is again evaporated and a second crop of alum crystals is obtained and removed; the mother liquor is now poured into a warm conc. aqueous solution of ammonium carbonate, the pp. (of Al_2O_3 &c.) is digested in contact with the liquid for four or five days and then filtered, the insoluble portion is again heated with $(NH_4)_2CO_3$Aq and the liquid is filtered off. The solution in $(NH_4)_2CO_3$Aq contains BeO, free, or almost free, from Al_2O_3, CaO, Fe_2O_3 &c.; the BeO may be obtained by boiling the solution (Nilson a. Pettersson, *B.* 11, 383), or by acidulating, boiling off CO_2, and ppg. by NH_3Aq (Hofmeister, *J. pr.* 76, 3); in either case, the ppd. $BeO.xH_2O$ should be again treated with $(NH_4)_2CO_3$Aq and then reppd. There are various other ways of

preparing $BeO.xH_2O$ from beryl (v. especially Joy, *J. pr.* 92, 232; Scheffer, *A.* 109, 146; Berzelius, *P.* 8, 187; Debray, *A. Ch.* [3] 44, 15).

Properties.—A white, loose, infusible powder; insoluble in, and unacted on by, water; soluble in acids and in molten KOH. According to Ebelmen (*A.* 80, 213) BeO is obtained in hexagonal crystals ($a:c = 1:1·587$) by cooling a solution of the oxide in molten boric acid; Debray obtained similar crystals of BeO by strongly heating ammonium-beryllium carbonate (*A. Ch.* [3] 44, 15). H. Rose described crystals of BeO obtained by heating the ordinary oxide in a porcelain oven (*Ph. C.* 1848. 486); S.G. of these crystals = 3·02.

Reactions and Combinations.—1. With most *acids* to form salts, *e.g.* $BeSO_4$, $Be.2NO_3$, &c.; the oxide becomes less easily soluble in acids by heating.—2. Decomposes molten *potassium carbonate* with evolution of CO_2; on addition of water BeO remains dissolved in the KOHAq.—3. Does not combine directly with *water*, but various hydrates, of which $BeO.H_2O$ is the most important, are obtained by the action of NH_3Aq on solutions of Be salts (*v.* BERYLLIUM, HYDROXIDES OF).

Beryllium, Oxychloride of. $Be_2OCl_2 = BeCl_2.BeO$. Said to be formed by evaporating an aqueous solution of $BeCl_2$.

Beryllium, Phosphide of. Described by Wöhler as a greyish powder obtained by heating Be in vapour of P; existence very doubtful as Wöhler's Be was very impure.

Beryllium, Salts of. Salts obtained by replacing H of acids by Be: they are generally obtained by the action of aqueous acids on $BeO.H_2O$. Most of the commoner salts—sulphate, nitrate, oxalate, chloride—are soluble in water and have a sweetish taste; the carbonate and phosphate are insoluble in water. When heated, the salts of Be are completely decomposed, except the acid be non-volatile. The chief salts of Be are the following (they are described under the headings CARBONATES, NITRATES, &c.) *carbonates, chromates, molybdates, nitrates, perchlorate, periodates, phosphates, selenate, selenites, silicates, sulphates.* The following salts probably exist, but few if any definite facts concerning them are known:—*bromate, chlorate, hypophosphite, iodate, phosphite, tungstate, vanadates.*

Beryllium, Selenide of. Existence very doubtful.

Beryllium, Silicide of. Be readily combines with Si; when Be is prepared in porcelain vessels a portion of the SiO_2 is reduced and as much as 20 p.c. Si may combine with the Be to form a hard, brittle mass. It is doubtful whether any definite compound of Be and Si has been obtained.

Beryllium, Sulphide of. Described by Wöhler (*P.* 13, 577) as a greyish fused mass, which evolves H_2S by action of acids; obtained by heating Be in S vapour. But existence is extremely doubtful; according to Fremy (*A. Ch.* [3] 38, 326) no sulphide of Be is produced by heating BeO in S, or CS_2, vapour. According to Nilson a. Pettersson (*B.* 11, 384), Be and S do not combine when heated together.

M. M. P. M.

BERYLLIUM, ORGANIC DERIVATIVES OF.

Beryllium ethide $BeEt_2$. (185°–188°). From $HgEt_2$ and Be at 130°. Takes fire in air (Cahours, *J.* 1873, 520).

Beryllium propide $BePr_2$. Does not take fire in air.

BETA.—Compounds beginning with *beta-* or *bet-* are described as β compounds under the word to which this prefix has been added.

BETAÏNE $C_5H_{11}NO_2$ *i.e.* $Me_3N{<}{\genfrac{}{}{0pt}{}{CH_2}{O}}{>}CO$.

Internal anhydride of the methylo-hydroxide of di-methyl-amido-acetic acid. S. 16 at 25°. In the hydrated condition $C_5H_{11}NO_2$ aq, it may be represented by the formula $Me_3N(OH).CH_2.CO_2H$.

Occurrence.—1. In the juice of beet-root (*Beta vulgaris*), and in beet-root molasses (Scheibler, *Z.* 6, 505; *B.* 3, 155; Liebreich, *Z.* 6, 506; *B.* 3, 161). The unripe root contains ·25 p.c.; the ripe root only ·1 p.c. The betaïne is not present in the root as such, but is liberated by treatment with HCl or baryta.—2. In mangold wurzel (Scheibler, *Z.* [2] 5, 539).—3. In cotton seed (Ritthausen, *J. pr.* [2] 30, 32).—4. In the leaves and branches of *Lycium barbarum* (Marmé a. Husemann, *A. Suppl.* 2, 383; 3, 245; *Ar. Ph.* [3] 6, 216).—5. In putrefying flesh (Gautier, *Bl.* [2] 48, 13).

Formation.—1. From tri-methyl-amine and chloro-acetic acid (Liebreich, *B.* 2, 13).—2. By oxidation of neurine $Me_3N(OH).CH_2.CH_2OH$. 3. Glycocoll (1 mol.) is dissolved in KOHAq and mixed with MeI (3 mols.) and MeOH; the liquid being kept alkaline (Griess, *B.* 8, 1406). 4. Silver glycocoll and MeI gives the iodide, $Me_3NI.CH_2.CO_2H$.

Preparation.—1. Diluted molasses are boiled for twelve hours with baryta; excess of baryta is removed from the filtrate by CO_2; the liquid is evaporated to a treacle and exhausted with alcohol; the alcoholic solution is treated with alcoholic $ZnCl_2$; the pp. is recrystallised from water, and decomposed by baryta; the barium is exactly removed from the filtrate by H_2SO_4, and betaïne hydrochloride crystallises on evaporation (Liebreich, *B.* 3, 161; *cf.* Scheibler, *B.* 2, 292; Frühling a. Schulz, *B.* 10, 1070).

Properties.—Large crystals (containing aq) (from alcohol). Ppd. as plates by adding ether to an alcoholic solution. Deliquescent. Over H_2SO_4 the crystals become $C_5H_{11}NO_2$. Sweet taste; neutral to litmus; inactive. Decomposed by heat, giving off odours of NMe_3 and of burnt sugar. Not affected by CrO_3 or HI. Fusion with potash gives off NMe_3. Iodine in KI pps. brown needles of a periodide.

Salts.—B'HCl or $Me_3NCl.CH_2.CO_2H$: monoclinic tables, v. sol. water.—$B'HAuCl_4$: plates or thin needles.—$B'_2H_2PtCl_6$ 2aq (R.).—$B'_2H_2PtCl_6$ 4aq (L.).—$(B'HCl)_2HgCl_2$.—$B'ZnCl_2$.—B'KI 2aq [139°] (Korner a. Menozzi, *G.* 13, 351).—B'KI [226°].—$B'_4H_2I_2(BiI_3)_2$ (Kraut, *A.* 210, 318).—$B'_2H_2SO_4$.

Methyl ether.—Iodide $INMe_3.CH_2.CO_2Me$. From silver glycocoll and MeI (Kraut, *A.* 182, 180).

BETH-A-BARRA COLOUR $C_{24}H_{26}O_5$. [135°]. A dye extracted from a West African wood (Sadler a. Rowland, *Am.* 3, 22). When dried at 100° it contains 3aq in the molecule.

BETORCIN $C_8H_{10}O_2$ *i.e.* $C_6H_2Me_2(OH)_2$ [1:4:3:5]. [163°]. (c. 279°). *β-Orcin. Di-oxy-p-xylene. Di-methyl-resorcin.*

Formation.—1. By boiling (β)-picroerythrin with baryta (Stenhouse, *A.* 68, 104; Lamparter, *A.* 134, 248; Menschutkin, *Bl.* 2, 428).—2. From amido-xylenol, $C_6H_2Me_2(NH_2)(OH)$ [1:4:3:5] by the diazo- reaction (Kostanecki, *B.* 19, 2321).

Preparation.—The lichen *Usnea barbata* is thoroughly extracted with cold water (10 pts.) and CaO (1 pt.), the extract is mixed with HCl. A pp. of usnic and barbatic acids is formed. This mixture (1 pt.) is boiled with water (40 pts.) and CaO (1 pt.) for four hours. An insoluble basic calcic usnate is formed while the barbatic acid splits up into CO_2 and betorcin. Air must be excluded, for betorcin oxidises very readily. The filtrate is at once neutralised with HCl, acidified strongly with acetic acid, evaporated (to 5 pts.) filtered from some tarry matter, and evaporated further to crystallisation. Recrystallised first from benzene, then from water. Yield $\frac{1}{16}$ per cent. (Stenhouse a. Groves, *C. J.* 37, 396).

Properties.—Less soluble in water than orcin. Gives a more crimson colour with hypochlorites than orcin does. Fe_2Cl_6 gives a green colour. Ammoniacal solutions turn red in air. Boiled with NaOH and chloroform it forms a red, non-fluorescent solution.

BETULIC ACID $C_{36}H_{54}O_6$. [195°]. From betulin and CrO_3 in HOAc (Hausmann, *A.* 182, 378). White powder, v. sl. sol. water, v. sol. alcohol.—$Pb_3(C_{36}H_{51}O_6)_2$.

BETULIN $C_{36}H_{60}O_3$. [251°]; [258° cor.] (Hausmann, *A.* 182, 369). S. (alcohol) ·7 at 15°; 4·2 at 78°. Occurs in the bark of the birch (Lowitz, *Crell. Chem. Ann.* 1788, i. 302; Hünefeld, *J. pr.* 7, 53; Hess, *J. pr.* 16, 161; Stähelin a. Hofstetter, *A.* 51, 79; Paterno a. Spica, *G.* 7, 508).

Preparation.—The bark is extracted with 96 p.c. alcohol, the alcohol evaporated and the residue after washing with water and with soda-solution is crystallised from benzene or naphtha, the crystals are finally decolourised with animal charcoal and recrystallised from alcohol (Franchimont, *B.* 12, 7).

Needles; may be sublimed. Insol. water, v. sl. sol. CS_2, sl. sol. alcohol and ether. At 130° it gives an Anhydride $C_{36}H_{58}O_2$. On distillation alone with powdered zinc, P_2O_5 or P_2S_5, hydrocarbons are produced of doubtful constitution.

Acetyl derivative $C_{36}H_{58}O(OAc)_2$ [216°].

BETULIN-AMARIC ACID $C_{36}H_{52}O_{16}$. From betulin and fuming HNO_3 (Hausmann, *A.* 182, 374). Crystals, v. sl. sol. water, v. e. sol. alcohol and ether. At 110° it gives the anhydride $C_{36}H_{50}O_{15}$ [181°].

Salts.—$K_4C_{36}H_{48}O_{16}$.—$CaBaC_{36}H_{48}O_{16}$.—$Ca_2C_{36}H_{48}O_{16}$.—$Pb_2C_{36}H_{48}O_{16}$.—$Cu_2C_{36}H_{48}O_{16}$.

Ethyl ether $Et_4C_{36}H_{48}O_{16}$. [117°].

BETULORETIC ACID $C_{36}H_{66}O_5$. [94°]. A white resin found on young birch-shoots and leaves (Kosmann, *J. Ph.* [3] 26, 197). Insol. water, v. sol. alcohol and ether. Oxidised by HNO_3 to picric acid.—$AgC_{36}H_{65}O_5$: flocculent pp.

BEZOAR.—A concretion found in the stomach or intestines of a variety of goat, *Capra ægragus*, or of the gazelle, *Antilope Dorcas*. They contain ellagic and lithopellic acids.

BICHROMATES, same as DICHROMATES, *q. v.* under CHROMIUM, ACIDS OF.

BICUHYBA FAT.—The fat of *Myristica bicuhyba* consists chiefly of the glycerides of myristic and oleic acids; it also contains small quantities of resins and free fatty acid (myristic acid), and a very small amount of an ethereal oil (Noerdlinger, *B.* 18, 2617).

BIEBRICH SCARLET *v.* p. 368.

BILE.—A liquid secreted by the liver. It is viscid, of green or brown colour, and has a bitter taste. S.G. about 1·02. Faintly alkaline. Possesses an emulsifying power like soap. Its composition varies. Ox-bile contains sodium glycocholate and taurocholate, cholesterin, urea, fats, salts of acetic and propionic acids, glyceryl tri-acetate, glyceryl tri-propionate, pigments, mucus, KCl, phosphates of Na, Ca, and Mg, and traces of iron, manganese, and silica. Human bile is of a similar composition.

Latschinoff (*B.* 18, 3039) has shown that saponified ox-gall contains, in addition to cholic acid (which is derived from the glyco- and tauro-cholic acids), a new acid to which he gives the name *choleic acid*. The latter acid, according to this investigator, occurs in two forms—*anhydrous* $C_{25}H_{42}O_4$ and *hydrated* $C_{25}H_{42}O_4 1\frac{1}{2}$ aq. Mylius (*B.* 19, 369) has found that cholic acid by putrefactive fermentation is reduced to a body (the '*desoxycholic acid*' of M.) which L. considers as identical with his so-called '*hydrated choleic acid.*' As however L. (*B.* 20, 1043) was unable to convert his 'anhydrous choleic acid' into the 'hydrated choleic acid' by any other method than by boiling with acetic acid and M. (*B.* 20, 1968) was unable to effect the conversion even in this way, there appears to be little doubt that these so-called 'anhydrous' and 'hydrated choleic acids' are quite distinct acids (the conversion by AcOH is probably erroneous). the latter being identical with the 'desoxycholic acid' of M. Hence the 'anhydrous' acid will be described as *choleic acid*, the 'hydrated' as *deoxycholic acid.* Both these acids according to L. give *dehydrocholeic acid* on gentle oxidation, and *cholanic acid* on more vigorous oxidation.

To *cholic acid* L. assigns the formula $C_{25}H_{42}O_5$, but M. (*B.* 19, 369, 2000; 20, 1968) has shown by a long series of careful analyses that, almost beyond a doubt, it is represented by the formula $C_{24}H_{40}O_5$ originally proposed for it by Strecker. On oxidation it first gives *dehydrocholic acid* $C_{24}H_{34}O_5$ and then *bilianic acid* $C_{24}H_{34}O_8$ (but no cholanic acid, which when obtained from cholic acid by earlier investigators, was due to the presence of choleic acid).

Pig's bile contains sodium hyoglycocholate and hyotaurocholate instead of glycocholate and taurocholate; it also contains glycero-phosphoric acid and neurine derived from the decomposition of lecithin. In other respects it resembles ox-bile. The various constituents of bile are separately described.

Pettenkofer's test. Bile, or an aqueous solution of a salt of bile, is mixed with two-thirds of its volume of H_2SO_4 and a drop of a 10 p.c. solution of sugar is added. On warming to 75° a crimson colour is produced. The reaction is

given by glycocholic, taurocholic, hyoglycocholic, hyotaurocholic, and by cholic acid (Pettenkofer, *A.* 52, 92; *cf.* Neukomm, *A.* 116, 30; Strassburg, *Pflüger's Arch.*, 4, 461). The test may be modified by using phosphoric acid. The substance to be tested, together with very little cane sugar, is dissolved in 3 drops of a mixture of syrupy phosphoric acid (5 vols.) and water (1 vol.) and the tube is then dipped into boiling water. A crimson colour soon appears (Kolbe, *J. pr.* [2] 27, 424). A red colour is produced by many other substances than those mentioned, hence it is necessary to confirm it by observing the absorption spectrum which contains three bands: one extending from midway between C and D to D, the second midway between D and E, and the third between B and F (Heynsius a. Campbell, *Pflüger's Arch.*, 4, 497; *cf.* Schenk, *Fr.* 12, 119).

BILE COLOURING MATTERS *v.* PIGMENTS, ANIMAL.

BILIANIC ACID

$C_{24}H_{34}O_8$ probably $C_{20}H_{31}(CO)_2(CO_2H)_3$.

Formed by further oxidation of dehydrocholic acid $C_{20}H_{31}(CO)(CHO)_2CO_2H$.

Preparation.—Cholic acid (20 pts.) in fine powder is added to a mixture of $K_2Cr_2O_7$ (40 pts.) and H_2SO_4 (60 pts.) in water (160 pts.), finally warming on the water-bath till the reaction is complete. It is isolated by conversion into the acid potassium salt, which is sparingly soluble in alcohol, and then into the di-ethyl-ether (Mylius, *B.* 20, 1981; *cf.* Clève, *Bl.* [2] 35, 373; Latschinoff, *B.* 19, 480; *Bl.* [2] 46, 818).

Properties.—Flat needles (containing $\frac{1}{4}$aq.). Tri-basic ketonic acid.

Salts.—$A''_2Ba_3$6aq or 8aq: tables or prisms. —$A'''HBa$2aq: hexagonal tables, sl. sol. water and alcohol.—Ag_3A'''.

Di-ethyl ether $A'''HEt_2$: [193°]; long flat needles; sol. alcohol, less sol. ether.—A'''_2Et_4Ba.—A'''_2Et_4Pb.

Tri-ethyl ether $A''Et_3$: [127°]; satiny tablets, or thick pillars.

Di-oxim $C_{19}H_{31}(C:NOH)_2(CO_2H)_3$. Formed by warming a slightly alkaline solution of bilianic acid with hydroxylamine. Glistening tables. Sol. dilute alcohol, nearly insol. water and absolute alcohol. Dissolves in alkalis, forming acid or neutral salts.

Di-phenylhydrazide

$C_{19}H_{31}(C:N_2HPh)_2(CO_2H)_3$: colourless needles. Nearly insol. acetic acid and hot alcohol, insol. water. Dissolves in alkalis.

iso-**Bilianic Acid** $C_{24}H_{34}O_8$ (?). [234°-237°]. Flat needles. Formed in small quantity, together with bilianic acid, by oxidation of cholic acid with $K_2Cr_2O_7$ and H_2SO_4.

Salts.—$A'''H_2K$: silky rhombic plates, sl. sol. water and alcohol.—$A'''Ag_3$: amorphous pp. —A'''_2Ba6aq: amorphous, sl. sol. water, insol. alcohol.

Methyl ether $A'''Me_3$: [98°]; needles (Latschinoff, *B.* 19, 1530).

BILIC ACID $C_{16}H_{22}O_6$. [about 190°]. Prepared by careful oxidation of cholic acid with chromic acid mixture (Egger, *B.* 12, 1468). White needles. Sol. hot water and alcohol, sl. sol. ether. Dibasic acid. It gives Pettenkofer's reaction with sugar and H_2SO_4. By oxidation it is converted into cholesteric acid ($C_{12}H_{16}O_7$).

BINARY THEORY OF SALTS. The name salt was given in ancient times to the solid residue obtained by boiling sea-water; it was then extended to include all solid substances easily soluble in water and obtainable by evaporating watery liquids. At a later time the possession of a taste more or less resembling that of sea-salt was regarded as a characteristic property of all salts. When the composition of the bodies called salts began to be studied, a threefold division was made into acid salts, alkaline salts, and neutral salts (*v.* ACID, ALKALI, SALT). Lavoisier's discovery of the nature of oxygen led to the definition of acids as highly oxygenated compounds; and Davy's decomposition of soda, potash, lime, and baryta, showed that these alkaline salts were also compounds of oxygen. But as neutral salts were formed by the mutual action of an acid and an alkali, it followed that they too were oxygenated compounds. A neutral salt, or we may say simply a salt, for the qualifying word neutral had been dropped by this time, was then regarded as constituted of two parts, an acid or electro-negative part, and a basic or electro-positive part. From this time dualistic views prevailed; every compound, said Berzelius, must be constituted of two parts, which may themselves be simple or complex, and of these parts one is positively and the other negatively electrified. Such a salt as sulphate of soda, for instance, was regarded as constructed of positive soda and negative sulphuric acid, rather than as formed by the mutual interaction of the elements sodium, oxygen, and sulphur. When, chiefly as a result of the work of Davy and Dulong, acids had come to be regarded as composed of the positive element hydrogen united with a negative element or group of elements, and salts were said to be formed by putting metals in the place of the hydrogen of acids, the conception of a salt as a binary structure still remained. One part of every salt was a positive element, a metal; the other part was a negative radicle, either a non-metal or a group of non-metallic elements.

In some such way as this arose the binary theory of salts, a theory which is based on the notion of every salt being a definite structure, and which conceives it possible to place all salts in one class, regard being had for classificatory purposes rather to the composition than to the properties of salt (*v.* CLASSIFICATION and SALTS). M. M. P. M.

BIRCH BARK. Contains betulin (*q. v.*) and a kind of tannin which is turned green by Fe_2Cl_6 (Stähelin a. Hofstetter, *A.* 51, 79).

BISMUTH. Bi. At. w. 208. Mol. w. probably 208 (*v.* Biltz a. Meyer, *Z. P. C.* 4, 249). [268°·3] (Rudberg, *P.* 71, 462; Riemsdyk, *C. N.* 20, 32). (1090°-1450°) (Carnelley a. Williams, *C. J.* 35, 565). S.G. $\frac{4°}{4}$ 9·759 (Schröder, *P.* 106, 226). S.G. liquid 10·055 (Roberts a. Wrightson, *A. Ch.* [5] 30, 274). S.G. is lowered by great pressure. S.H. (20°-48°) ·0305 (Kopp, *T.* 155, 71); (9°-102°) ·02979 (Bède, *Mém. B.* 1855-56. 28); (liquid 280°-380°) ·0363 (Person, *A. Ch.* [3] 24, 129). C.E. (12°-41°) ·001333 (Kopp, *A.* 81, 1); (0°-100°) ·001316 (Matthiessen, *Pr.* 15, 220; *v.* also Fizeau, *P.* 135, 372; 138, 267). Ht. of fusion at 266°·8 = 12,640 (Person, *A. Ch.* [3] 24, 129). T. C. (Ag = 100) 1·8 (Wiedemann

a. Franz, *P.* 89, 497). E. C. at 0° (Hg at 0° = 1) ·8676 (Lorenz, *W.* 13, 422, 582). Cryst. form, hexagonal, $a:c = 1:1·3035$; isomorphous with Te, As, Sb. S.V.S. abt. 21·3. H.C. $[Bi^2, O^3]$ abt. 95,500 (Woods, *P. M.* [4] 4, 370). Emission-spectrum characterised by very many lines; in arc-spectrum the predominant lines are 4722·1, 4119, 3595·3, 3510·4, 3396·2, 2593, 2524, 2400·8, 2277 (Liveing a. Dewar, *T.* 174, 187, *v.* also, regarding spectrum of Bi, Hartley a. Adeney, *T.* 1884. 63).

Occurrence. Uncombined with other elements, in Saxony and other parts of Germany, in Norway, Spain, California, and in Cornwall and Cumberland, &c. Also as Bi_2O_3 (*Bismuth ochre*), Bi_2S_3 (*Bismuth glance*), Bi_2Te_3, $Bi_2Cu_2S_3$, $Bi_2Pb_2S_5$, &c., &c. Bismuth has been known for many centuries; Basil Valentine (15th century) seems to have been the first to recognise it as a definite metallic body Bergmann gave the earliest fairly accurate account of its reactions.

Formation.—Native bismuth is melted in iron tubes, and the metal is run off from gangue &c. into pots. By remelting with $\frac{1}{10}$ of its weight of KNO_3, at as low a temperature as possible, until the nitre forms a solid slag on the surface, approximately pure Bi is obtained.

Preparation. Approximately pure metal is dissolved in the minimum quantity of HNO_3Aq, much water is added, the pp. of basic nitrate is washed, boiled twice with pure KOHAq, or NaOHAq (Herapath, *D. P. J.* 169, 40), dissolved in as little HNO_3Aq as possible, and water is again added. The pp. is washed, dried, mixed with *black flux* (obtained by heating cream of tartar in a closed vessel) and heated at about 270°–280° in a closed crucible. The reduced metal is washed in dilute HClAq, and in water, and dried. Traces of As, Sb, or Fe, which yet remain in the metal are removed by partially oxidising and melting under the small quantity of Bi_2O_3 formed: this may be effected (1) by adding a little pure KNO_3, melting in an open porcelain crucible, keeping molten for some time, allowing to cool until a small quantity of the metal solidifies, and pouring off the still molten metal from the more solid oxides on the surface; (2) by melting under Na_2CO_3 containing 2·5 p.c. $KClO_3$ and proceeding as in (1) (Türach, *J. pr.* [2] 14, 309); (3) by strongly heating with 1 part cream of tartar, then running the molten metal (which contains K) into a crucible containing charcoal, heating for a little, running into an open porcelain vessel, strongly heating in air for some time, and finally pouring off the molten metal from the slag on the surface (Mehu, *D. P. J.* 211, 187). Löwe (*Fr.* 22, 498) recommends ppn. of $Bi3NO_3$ in HNO_3Aq by KOH, solution of pp. in excess of KOH in presence of glycerine, addition of grape sugar, filtration from Ag and Cu, and boiling; pure Bi is ppd. Bi is obtained in well-formed crystals by melting the commercial metal with a little KNO_3 in a crucible until a small quantity taken out appears yellow on the surface (indicative that foreign metals are oxidised), removing the scum of oxides from the surface, covering the molten mass with pieces of charcoal (to prevent oxidation), allowing to cool until a firm crust has formed, piercing two holes in the crust, and pouring off the still molten metal; the crucible is found to be lined with crystals of Bi.

Properties.—Very lustrous; white with a slightly reddish tinge; very easily crystallises; brittle; diamagnetic, but not so when molten (Faraday, *P. Suppl.* 3, 1; Weber, *P.* 73, 241; 87, 145; Reich, *P.* 97, 283; Plücker, *P.* 72, 339; 76, 576; 81, 133). For thermo-electric behaviour *v.* Svanberg, *C. R.* 31, 250; Franz, *P.* 83, 374; Matteucci, *C. R.* 40, 541. Bi expands as it solidifies (for method of demonstrating this *v.* Böttger, *D. P. J.* 212, 441). May be distilled at a high temperature (over 1100°) in an atmosphere of H. The atom of Bi is trivalent in the gaseous molecule $BiCl_3$. Bi forms numerous alloys most of which melt at low temperatures, and expand on solidification (*v.* BISMUTH, ALLOYS OF). The atomic weight of Bi has been determined (1) by finding V.D. of, and determining Cl in, $BiCl_3$ (Dumas, *A. Ch.* [3] 55, 129 a. 176); (2) by oxidising Bi to Bi_2O_3 by means of HNO_3 (Schneider, *P.* 82, 303; *J. pr.* [2] 30, 237; Löwe, *Fr.* 22, 498; Marignac, *A. Ch.* [6] 1, 289); (3) by converting Bi_2O_3 into sulphate (Marignac, *l. c.*). The exact value to be given to the at. w. of Bi is still doubtful; it is certainly not greater than 208. Bi is metallic in its chemical functions; it shows a marked tendency to form basic rather than normal salts; many of these basic salts may be represented as containing the group BiO *e.g.* $BiO.NO_3$, $(BiO)_2SO_4$, &c.; several oxychlorides and oxybromides are known; no hydride of Bi has yet been obtained; the oxides of Bi are salt-forming in their reactions with acids, none of them is an anhydride, but moist Bi_2O_5 dissolves in very conc. boiling KOHAq probably with formation of compounds in which Bi acts as part of the negative radicle (*v.* BISMUTHIC OXIDE under BISMUTH, OXIDES OF). Bi shows distinct analogies to As and Sb, also to the other members of Group V., in its chemical relations; for fuller discussion *v.* BISMUTH, CHEMICAL RELATIONS OF. Bi salts are used in medicine: the alloys are used in printing, soldering, &c.

Reactions.—1. Very superficially oxidised in ordinary *air*: heated in air or *oxygen* burns to Bi_2O_3.—2. Decomposes *steam* at a red heat.—3. Combines directly with several *elements*, especially O, Cl, Br, I, S, Se, and Te: $[Bi,Cl^3]$ = 90,630 (*Th.* 2, 410); $[Bi^2,O^3]$ = abt. 95,000 (Woods, *P. M.* [4] 4, 370).—3. Scarcely acted on by *hydrochloric acid* dilute or conc.—4. With hot conc. *sulphuric acid* a basic sulphate is formed.—5. Quickly dissolved by *nitric acid* with formation of $Bi.3NO_3$.—6. Oxidised, but slowly and partially, by fusion with *potassium nitrate* or *chlorate*.

Estimation.—Generally as Bi_2O_3, after ppn. from a solution free from HCl and chlorides by excess of ammonium carbonate, and warming for some time; the pp. is washed, dried, and heated whereby Bi_2O_3 is produced. Also by adding much water to a solution in as little HCl as possible, warming, collecting BiOCl, and drying at 100°–110° (traces of Bi remain unppd.); the BiOCl may be reduced by heating with KCN, and the Bi weighed. Ppn. as Bi_2S_3 and weighing is not to be recommended, as Bi_2S_3 is easily oxidised in moist air. Volumetric

methods of estimating Bi, none of which however is altogether satisfactory, have been based on (1) ppn. of $Bi(IO_3)_3$ from acetic acid solutions by a measured mass (excess) of HIO_3Aq, and determination of residual HIO_3 (Buisson a. Ferray, *M. S.* [3] 3, 900); (2) ppn. of Bi chromate from nearly neutral solutions by K_2CrO_4Aq or $K_2Cr_2O_7Aq$; (3) pptn. of Bi phosphate by standardised Na_2HPO_4Aq; (4) ppn. of Bi oxalate, conversion into basic oxalate by boiling water, and titration with $K_2Mn_2O_8Aq$; (5) ppn. of double oxalate of Bi and K by standardised $K_2C_2O_4Aq$ and determination of residual $K_2C_2O_4$ by $K_2Mn_2O_8Aq$ (Pattison Muir, *C. J.* 29, 483; 32, 674; 33, 70; (with Robbs) *C. J.* 41, 1).

Chemical Relations of Bismuth.—Bi is the highest known member of Group V.; this group contains the following elements:—

Even series	2	4	6	8	10	12
	N=14	V=51	Nb=94	Di=142	Ta=182	—
Odd series	3	5	7	9	11	13
	P=31	As=75	Sb=120	Er=166	Bi=208	—

Taken as a whole these elements are negative and their compounds with H and O react as acids. As the group is ascended the negative characters become less marked until Bi is reached; omitting N, the oxides M_2O_3 of the even series members, so far as known, are salt-forming in their reactions with acids; but in the odd series members these oxides, on the whole, are salt-forming only in their reactions with bases, until Series 9 is reached, when the character of the oxides M_2O_3 becomes decidedly basic. The oxides M_2O_5, on the whole, are acid-forming, but the acidic functions of Bi_2O_5 are very feeble. Salts formed from acids by replacement of H are obtained in the cases of V, Di, Er, and Bi; but most of the salts of vanadium, and many of those of Bi, seem to contain groups of the form M_2O_2, acting as the more positive part of the salt; several salts of the normal type, *e.g.* $Bi.3NO_3$, are however known and several normal Er and Di salts have been prepared. Vanadium is characterised by the great number of complex compounds into which it enters, sometimes as part of the positive, sometimes as part of the negative, group of the salt. Considering the compositions of the haloid, and oxyhaloid compounds, we find that, so far as investigation has gone, compounds of the form MX_3 and MOX_3, where X = a halogen element, exist when M is any member of the group except Bi or As (N is omitted as there is much doubt concerning the composition of its haloid compounds), and in the case of As compounds of AsF_5 with KF, &c., seem to exist; the compounds $BiBr_2(C_6H_5)_3$ and $BiCl_2(C_6H_5)_3$ are known as solids (Michaelis, *B.* 20, 52). The haloid compounds BiX_3 are less easily oxidised than the corresponding compounds of P, As, or Sb. The basic character of the oxides of bismuth, the existence of many salts in which Bi acts as the metallic element, the stability of the haloid compounds BiX_3 and the non-existence of BiX_5, the non-existence of any compound in which Bi_2S_3 acts as the negative radicle; these, among other properties, show that Bi must be classed as the distinctly metallic element of Group V. But the feebly acidic functions of Bi_2O_5 towards strong alkalis, the readiness with which so-called basic salts of bismuth are formed, the fact that Bi_2O_4 and Bi_2O_5 form no corresponding salts, the existence of several complex oxyhaloid compounds; these, among other properties, show that the general non-metallic character of Group V. to some extent belongs to Bi.

Bismuth, Alloys of. Bismuth alloys with many metals when melted with them; these alloys are characterised by low melting points, and, many of them, by the expansion which they undergo as they cool after being melted. The most technically important alloys are:—*Newton's metal*; 8 parts Bi, 5 Pb, and 3 Zn, M.P.=94°·5: *Rose's metal*; 2 Bi, 3 Pb, 2 Sn, M.P.=91°·6: *Wood's metal*; 15 Bi, 8 Pb, 4 Sn, 3 Cd, M.P.=68°: *Fusible metal*; 2 parts Bi, 1 Pb, 1 Sn, M.P.=93°·7; this alloy expands from 32° to 95°, contracts gradually to 131° when its volume is less than at 32°, then expands to 174°, after which its expansion is uniform.

Amalgams of Bi are easily formed at ordinary temperatures. Alloys with *copper* are formed below the melting point of Cu; an alloy of 2 parts Bi with 1 part Cu begins to expand after solidification (Marx, *S.* 58, 470). An alloy of 3 parts Bi with 1 part *iron* is magnetic. Alloys of Bi and *palladium* are hard as steel; with ½ part spongy *platinum* Bi forms an easily fusible alloy which separates into Pt and Bi when fused at a low red heat. Bi does not alloy with *zinc*; on mixing melted Zn and Bi two layers are formed, one containing a little Bi and much Zn, the other much Bi and little Zn.

Bismuth, Bromides of. Only one bromide, $BiBr_3$, has been obtained with certainty; but many facts point to the existence of a lower bromide, probably $BiBr_2$.

TRIBROMIDE. $BiBr_3$. (*Bismuthous bromide.*) Mol. w. unknown, but probably as represented by formula. [210°-215°] (Pattison Muir, *C. J.* 29, 144). (Between 454° a. 498°) (Carnelley a. Williams, *C. J.* 33, 283).

Formation.—1. By heating powdered Bi in CO_2 charged with Br vapour.—2. By adding powdered Bi to a solution of Br in dry ether, and evaporating *in vacuo*.

Preparation.—1½ parts Br are allowed to flow, in small successive quantities, into 1 part powdered Bi in a small retort with the beak tilted upwards; when the mass is cool, the retort is *very gently* warmed for some days, and from time to time a few drops of Br are poured into the retort; the bromide forms in yellow crystals a little distance above the heated mass.

Properties and Reactions.—Golden yellow crystals; S.G. $\frac{20}{20}$ 5·4; very deliquescent; soluble in dry ether; decomposed by *water* to BiOBr and HBrAq; partially reduced to Bi by heating in *hydrogen*; heated with Bi_2O_3 forms BiOBr; by action of *nitrogen oxides* obtained by heating starch with HNO_3Aq the oxybromide $Bi_8O_{11}Br_2$ is produced; unchanged when heated in CO_2 or SO_2; reacts with *ammonia*, when heated in that gas, to form (1) $BiBr_3.3NH_3$, which is a straw-yellow powder, soluble in HClAq and yielding $BiBr_3.3NH_4Cl.H_2O$ by evaporation over H_2SO_4; (2) probably $BiBr_3.2NH_3$, an olive-green solid; (3) an ash-grey, crystalline, infusible, solid, probably BiN_2Br. The compound $2BiBr_3.5NH_3$ is

obtained (along with Bi), as a greyish-green powder, by heating $Bi_4O_4Br_2$ to dull redness in dry NH_3 (Pattison Muir, *C. J.* 29, 144; 16, 27). A solution of $BiBr_3$ in saturated KClAq deposits crystals of $BiCl_3Br_2K_2.1\frac{1}{2}H_2O$ (Atkinson, *C. J.* 43, 292). Does not combine with Cl.

DIBROMIDE.—Probably $BiBr_2$ or Bi_2Br_4. In preparing $BiBr_3$ dark grey crystals are formed if there is a deficit of Br; these contain Br nearly agreeing with the formula $BiBr_2$; on heating they give Bi and $BiBr_3$. Weber (*P.* 107, 599) obtained a brown mass—probably a lower bromide than $BiBr_3$—by heating $BiBr_3$ with Bi; Macivor (*C. N.* 30, 190) obtained a dark grey solid, melting at 198°-200°, by heating Bi and Br.

Bismuth, Chlorides of. Two chlorides are known, $BiCl_3$ and Bi_2Cl_4: all attempts to form a chloride with more Cl than $BiCl_3$ have failed. Both may be obtained by the direct combination of Bi and Cl; Bi_2Cl_4 is separated into $BiCl_3$, Bi, and Cl, by heating; $BiCl_3$ is reduced to Bi_2Cl_4 by heating with Bi, or with Hg_2Cl_2.

TRICHLORIDE. $BiCl_3$ (*Bismuthous chloride*). Mol. w. 314. [227°] (Pattison Muir, *C. J.* 29, 144). (427°-439°) (Carnelley a. Williams, *C. J.* 33, 281).

Formation.—1. By heating 1 part powdered Bi with 2 parts $HgCl_2$ in a retort.—2. By dissolving Bi_2O_3 in HClAq, evaporating to dryness, heating in air and then in a retort.—3. By heating Bi_2O_3 in dry Cl.

Preparation.—Powdered Bi is heated in a current of dry Cl, in a retort with the beak tilted upwards and furnished with an exit tube passing into conc. H_2SO_4; when a light yellow liquid has been formed, the stream of Cl is slackened and the retort is very gently heated for some time; crystals of $BiCl_3$ sublime on to the upper parts of the vessel. The crystals may be distilled into small tubes in a current of dry N; the tubes are at once sealed.

Properties and Reactions.—White, very deliquescent, crystals, melting in Cl to a pale yellow liquid; S.G. $\frac{11°}{}$ 4·56; soluble in dry alcohol. Heated in *air* between two watch glasses part sublimes and an oxychloride—$Bi_4O_3Cl_6$ or $Bi_4O_4Cl_4$—remains. The same oxychloride is obtained by the action of *nitrogen oxides* (from starch and HNO_3Aq) on $BiCl_3$. Heated in *hydrogen* Bi_2Cl_4 and Bi are formed, at a higher temperature all the Cl is removed. Decomposed by *water* to BiOCl and HClAq; the amount of change depends on the relative masses of $BiCl_3$, HCl, and H_2O, and on the time; when the reacting bodies are mixed in the ratio $BiCl_3$: 26HCl: 10,000 H_2O a little $BiCl_3$ remains unchanged even after 14 days action (*v.* Pattison Muir, *C. J.* 35, 311; Ostwald, *J. pr.* [2] 12. 264). Heated with *sulphur* BiSCl is formed (*v.* BISMUTH SULPHOCHLORIDE). Not acted on by CrO_2Cl_2; scarcely acted on by SO_2; does not combine with Br (P. M., *C. J.* 39, 33).

Combinations.—With *ammonia* to form (1) $2BiCl_3.NH_3$, a red, fusible, crystalline, solid; (2) $BiCl_3.2NH_3$, a greenish solid; (3) $BiCl_3.3NH_3$, a white, volatile solid (Déhérain, *C. R.* 54, 724). These ammonio-chlorides by treatment with HClAq yield compounds of the form $xBiCl_3.yNH_4Cl$, where x varies from 1 to 2, and y from 1 to 5. With *potassium chloride* forms $BiCl_3.2KCl.2\frac{1}{2}H_2O$; also with *sodium chloride* forms corresponding salt with $3H_2O$; a solution of $BiCl_3$ in *hydrochloric acid* when evaporated gives needles of $BiCl_3.2HCl$ (Jacquelain, *A. Ch.* [2] 62, 363).

DICHLORIDE.—Probably Bi_2Cl_4. Mol. w. unknown.

Formation.—1. By gently heating $BiCl_3$ in H; but the product is mixed with Bi and $BiCl_3$. 2. By heating $BiCl_3$ with Bi (Weber, *P.* 107, 596).—3. By heating $BiCl_3.xNH_4Cl$ in H to 300° (Schneider, *P.* 96, 130).

Preparation.—A very intimate mixture of 2 parts HgCl with 1 part extremely finely powdered Bi is heated to 230°-250° in a closed tube for some time; the mixture melts to a dark brownish black liquid, and Hg (with a little Bi) collects at the bottom of the tube; the sides of the tube are tapped from time to time to make the Hg settle; after cooling the Bi_2Cl_4 solidifies over the Hg, it is removed as quickly as possible to another tube—which is at once closed—and again melted; this process is repeated several times; nearly pure Bi_2Cl_4, containing a very little Hg and Bi, is finally obtained (Schneider, *P.* 96, 130).

Properties and Reactions.—Black, or nearly black, extremely deliquescent, solid; with *water* forms BiOCl; with *potash* gives Bi_2O_2 which is quickly oxidised to $Bi_2O_3.xH_2O$; with dilute mineral acids gives Bi salts and Bi; heated to about 300° gives $BiCl_3$ and Bi.

Bismuth, Cyanides and Ferrocyanides of, *v.* CYANIDES.

Bismuth, Fluoride of. Only one fluoride of Bi has as yet been prepared (Pattison Muir, Hoffmeister and Robbs, *C. J.* 39, 33), BiF_3. Mol. w. unknown.

Preparation.—1. Bi_2O_3 is added in small successive quantities to HFAq heated in a Pt dish until the oxide ceases to be dissolved; the liquid is decanted and evaporated at 100°; the residue, $BiF_3.3HF$, is warmed at about 110°-120° in a closed Pt crucible until dry, and is then heated (in the closed crucible) so long as HF is evolved.—2. Excess of saturated KFAq is added to a solution of $Bi(NO_3)_3$ in the minimum quantity of dilute HNO_3Aq, the pp. is thoroughly washed with boiling water, dried at 100°, and heated to dull redness in a closed Pt crucible.

Properties.—Grey, heavy, crystalline, solid. S.G. $\frac{20}{0}$ 5·33. Unacted on by *water*; insoluble in *alcohol*; scarcely changed or volatilised by heating to redness in open Pt dish; not oxidised by heating in nitrous oxides (from starch and HNO_3Aq); dissolved, with decomposition, by hot HCl, HNO_3, or H_2SO_4Aq. Combines with HF to form $BiF_3.3HF$ (*v. supra*) which is a crystalline, greyish-white, deliquescent solid, decomposed by boiling water to BiOF (*v.* BISMUTH OXYFLUORIDE).

Bismuth, Haloid Compounds of. BiF_3; $BiCl_3$, Bi_2Cl_4; $BiBr_3$ (? Bi_2Br_4); BiI_3. The V. D. of $BiCl_3$ only has been determined; the other formulæ are probably molecular. Bi_2Cl_4 and Bi_2Br_4 are decomposed by heat to Bi and BiX_3; the others are unchanged when heated out of air; heated in air all except BiF_3 are more or less oxidised, $BiCl_3$ to the greatest, and BiI_3 to the least, extent. BiI_3 is a very stable com-

pound (*v.* BISMUTH, FLUORIDE OF; CHLORIDES OF; BROMIDES OF; and IODIDE OF).

Bismuth, Hydrated oxides, or hydroxides of, *v.* BISMUTH, OXIDES OF.

Bismuth, Iodide of. BiI_3. Mol. w. unknown; probably as represented by formula.

Formation.—1. By heating an intimate mixture of 1 part Bi_2S_3 with 1¼ parts I, in a large, loosely covered flask, and then heating the sublimed BiI_3 at 100° to remove I (Schneider, *P.* 99, 470).—2. By dropping $Bi3NO_3$ in dilute HNO_3Aq into conc. KIAq, dissolving the brown pp. in fairly conc. HIAq, and ppg. BiI_3 by as little water as possible (Rammelsberg, *P.* 48, 166), drying pp. at 100°, and removing free I by one or two washings with absolute alcohol.—3. By the action of HIAq on Bi_2O_3.

Preparation.—An intimate mixture of 1 part Bi with 2 parts I is gently heated in a flask with a long neck passing into another flask; the sublimate is finely powdered and again heated in the same way as before; this is repeated once or twice; and finally the mass is distilled in a fairly rapid current of dry CO_2 (Weber, *P.* 14, 113 [slightly modified]).

Properties and Reactions.—(Pattison Muir, Hoffmeister a. Robbs, *C. J.* 39, 33.) Dark grey, metal-like, lustrous, crystal- (probably hexagonal, Nicklès, *C. R.* 50, 872); S.G. 5·65. S. (alcohol at 20°) *c.* 3·5. Unchanged in *air*; heated in air a very little Bi_2O_3 is formed. Unchanged by heating in *hydrogen*, or with *sulphur*, or in *sulphur dioxide*. Slowly changed to BiOI by a large quantity of cold *water*, more quickly by boiling water. Very partially converted into BiOI by heating in N oxides (from starch and HNO_3Aq). BiI_3 is much more stable than either $BiCl_3$ or $BiBr_3$.

Combinations.—With HI to form $BiI_3.HI.4H_2O$ (Arppe, *P.* 44, 248). With MI (M = Na, K, NH_4), and MI_2 (M = Ca, Ba, Mg, Zn), to form double compounds isomorphous with the corresponding compounds of SbI_3: obtained by direct combination of the iodides, or by acting on Bi with I in presence of the iodide MI or MI_2; they are all deliquescent, and are easily resolved by water into their component iodides (Nicklès, *C. R.* 51, 1097; Linan, *P.* 111, 240).

Bismuth, Oxides and hydrated oxides of. Four oxides are known, Bi_2O_2, Bi_2O_3, Bi_2O_4, Bi_2O_5; as none has been gasified, the V.D. and hence the molecular weight of none is known. These oxides all react with acids to form the same series of salts, BiX_3, where $X = NO_3, \frac{SO_4}{2}, \frac{CO_3}{2}$, &c.; if much water is present, basic salts, usually of the form BiOX, are produced; in the reactions of Bi_2O_2 with acids Bi is separated as metal; in the reactions of Bi_2O_4 and Bi_2O_5 oxygen is evolved. $Bi_2O_5.xH_2O$ is slightly soluble in very conc. boiling KOHAq, but no salts have been certainly obtained in which the acid radicle is composed of Bi and O. Bi_2O_2 is easily oxidised to Bi_2O_3; Bi_2O_4 and Bi_2O_5 are deoxidised to Bi_2O_3 by heating in air or oxygen to about 320° and 250° respectively; Bi_2O_3 is unchanged when heated in air or oxygen. Bi_2O_3 is not hydrated by contact with water; Bi_2O_4 and Bi_2O_5 are hydrated in moist air, in contact with water they are partially and slowly deoxidised to hydrates of Bi_2O_3.

The more important papers on the oxides and hydrated oxides of Bi are as follows:—1. On oxides containing less O than Bi_2O_3:—Thomson (*Proc. Glasgow Phil. Soc.* 1841-43, 4); Heintz (*P.* 63, 55, 559); Schneider (*P.* 88, 49; 97, 480); Arppe (*P.* 64, 237); Vogel (*Kastner's Archiv*, 23, 86); Berzelius (*Lehrbuch*, 2, 574 [5th ed.]); Schiff (*A.* 119, 331); Pattison Muir (*C. J.* 32, 128).—2. On oxides containing more O than Bi_2O_3:—Jacquelain [1838] (*J. pr.* 14, 1); Heintz [1844] (*P.* 63, 559); Arppe [1845] (*P.* 64, 237); Böttger [1858] (*J. pr.* 73, 494); Schröder [1862] (*A.* 121, 204); Boedeker [1862] (*A.* 123, 61); Wernicke [1870] (*P.* 141, 109); C. Hoffmann, [1884] (*A.* 223, 110); Pattison Muir [1876 to 1886] (*C. J.* 29, 144; 31, 24; 32, 128; *ibid.* 39, 21 [with Hoffmeister a. Robbs]; 51, 77 [with Carnegie]); Hasebrock [1887] (*B.* 20, 213).—3. On Bi_2O_3:—Bonsdorff (*P.* 41, 305); Fuchs (*S.* 67, 429); Stromeyer (*P.* 26, 553); Liebig (*Mag. Pharm.* 35, 114); Pattison Muir (*l.c.*).

HYPOBISMUTHOUS OXIDE. Bi_2O_2 (*Bismuth suboxide. Bismuth dioxide. Black oxide of bismuth*).

Preparation.—A mixture of 1 part $SnCl_2$ and 2·5 parts Bi_2O_3 is dissolved in as little fairly conc. HClAq as possible, the solution is poured into an excess of KOHAq (about 1 KOH in 10Aq) in a stoppered flask so that the flask is nearly filled with the liquid; the stopper is placed in the flask, and the black pp. is allowed to settle; the pp. is washed with cold KOHAq (in air-free water) less concentrated than that used in the ppn. the flask being each time nearly filled with the liquid, and then with air-free water; it is then quickly dried by pressing between filter paper, and placed over H_2SO_4 *in vacuo* (Schneider, *P.* 88, 45).

Properties and Reactions.—Black, crystalline, powder; begins to oxidise in air at about 180°; at red heat quickly oxidised to Bi_2O_3; oxidised to $Bi_2O_4.xH_2O$ and $Bi_2O_5.xH_2O$ by boiling with KOHAq and Br; oxidised to $Bi_2O_4.xH_2O$ by $K_2Mn_2O_8Aq$; when moist, Bi_2O_2 is rapidly oxidised in air to $Bi_2O_3.2H_2O$; oxidised by contact with a very little HNO_3Aq, decomposed to $Bi_2.6NO_3$ and Bi by more HNO_3Aq, dissolved entirely by a considerable quantity of the same acid; decomposed by HClAq or H_2SO_4Aq to $BiCl_3$, or Bi sulphate, and Bi; deoxidised, to Bi, by heating in H or CO; decomposed by boiling KOHAq with formation of Bi (Schneider, *l.c.*; Pattison Muir, *l.c.*). No hydrate of Bi_2O_2 has been definitely obtained. Solution of Bi_2O_2 in tartaric acid is said to give Bi_2S_2 by reaction with H_2S (Schneider), *v.* BISMUTH DISULPHIDE.

BISMUTHOUS OXIDE. Bi_2O_3 (*Bismuth trioxide*). S.H. (12°-97°) ·0609 (Regnault, *A. Ch.* [3] 1,129). S.G. 8·21 (Herapath, *P. M.* 64, 321); 8·08 (Playfair a. Joule, *C. J. Mem.* 3, 57). Occurs native generally associated with oxide of iron.

Formation.—1. By heating Bi in air or O.—2. By ppg. Bi nitrate or chloride solution by excess of alkali and boiling; thus prepared always contains some oxynitrate or oxychloride.

Preparation.—1. Basic Bi nitrate, obtained by ppg. solution of Bi in HNO_3Aq by large excess of water, is heated in a Pt dish with constant agitation until oxides of N are no longer evolved. If this oxide is fused with KOH it crystallises on cooling in rhombic

prisms, $a:b:c = \cdot 8165:1:1\cdot 064$ (Nordenskjöld, *P.* 114, 512).—2. BiOCl (*q.v.*) is shaken for some time with very conc. KOHAq, until the change to Bi_2O_3 and KCl is complete; the Bi_2O_3 is washed with cold water until quite free from KOH and KCl and dried: the oxide may be thus obtained in distinct crystals.

Properties and Reactions.—Heavy, yellowish-white, solid; unchanged by heating in *air* or *oxygen*. Dissolves in *acids* to form Bi salts (*v.* BISMUTH, SALTS OF). HFAq heated with Bi_2O_3 dissolves part of it as $BiF_3.3HF$ and converts the rest into $BiOF.2HF$; HXAq (X = Cl or Br) added to Bi_2O_3 little by little converts the whole of the Bi into BiOX, on addition of more HXAq the BiOX dissolves as BiX_3; with a little HIAq BiI_3 is alone formed, if very dilute HIAq is added and the temperature is raised BiOI only is produced, with considerable excess of fairly conc. HIAq BiI_3 is formed and dissolved. Heated in *chlorine*, $BiCl_3$ is formed; with *bromine* $BiBr_3$ and $Bi_{11}O_{15}Br_3$ are produced. Heated in *carbon monoxide* reduction begins at about 200°, and in *hydrogen* at about 240°. Bi_2O_3 is not hydrated in *moist air*; nor is it altered by contact with *water*. Unchanged by heating in *nitrogen*. *Oxidised* to Bi_2O_4 and Bi_2O_5 by action of chlorine in presence of much hot KOHAq; scarcely oxidised by $K_2Mn_2O_8Aq$ (*v.* further HYPOBISMUTHIC, and BISMUTHIC, OXIDE).

HYDRATED BISMUTHOUS OXIDE. $Bi_2O_3.xH_2O$; $x = 1$, 2, and 3. The hydrate with $2H_2O$ is obtained by dissolving $Bi_2O_3.xH_2O$ in conc. HClAq, ppg. by KOHAq, and drying over H_2SO_4 *in vacuo*: the hydrate with H_2O is obtained by dissolving $Bi_2O_3.xH_2O$ in conc. H_2SO_4, reducing by SO_2, ppg. by KOHAq, and drying as before (P. M., *C. J.* 32, 131). $Bi_2O_3.3H_2O$ is very difficult to obtain quite free from oxy-salts and Bi_2O_4; pps. formed by adding KOHAq to Bi_2O_3 in HCl, HNO_3, or H_2SO_4, and washing with cold water, always contain basic chloride, &c.; if washed with hot water they contain Bi_2O_4. Nearly pure $Bi_2O_3.3H_2O$ is obtained by dissolving Bi_2O_3 in the minimum of HNO_3Aq, pouring into excess of conc. NH_3Aq, washing with cold water until the washings contain no nitrates, then repeatedly agitating with *very dilute* Na_2CO_3Aq (to decompose traces of basic nitrates), again washing repeatedly with cold water, and drying *in vacuo* over H_2SO_4. The hydrates of Bi_2O_3 are white solids, easily dehydrated by heat, partially even by contact with hot water; Bi_2O_3 does not directly combine with water. The hydrates behave towards acids and oxidisers similarly to Bi_2O_3. None of these hydrates shows the slightest indications of acidic functions. Thomsen gives the thermal values $[Bi^2, O^3, 3H^2O] = 137,740$; $[BiO^3H^3, HClAq] = 14,130$, with formation of $BiOCl + 2H_2OAq$ (*Th.* 2, 244).

HYPOBISMUTHIC OXIDE, AND HYDRATES, Bi_2O_4; $Bi_2O_4.H_2O$; $Bi_2O_4.2H_2O$ (Arppe, Schröder, Böttger, Wernicke, Pattison Muir). *Preparation of Bi_2O_4.*—Bi_2O_3 is suspended in KOHAq, S.G. abt. 1·35, the liquid is kept nearly boiling, and Cl is passed in until the solid is dark chocolate-red and quite homogeneous to the eye; the solid is washed with hot water until the washings are neutral to litmus, kept in contact with dilute **HNO_3Aq (1 conc. acid to abt. 20 water) until the colour of the solid has become brownish-yellow (12–16 hours) (to dissolve any Bi_2O_3 and reduce any Bi_2O_5), washed free from acid, and boiled with conc. NaClOAq (to reoxidise any traces of Bi_2O_3) until a heavy, yellow-brown, powder is** formed which settles quickly; this powder is washed with hot water until quite free from alkali and Cl, and dried at 180°.

Hydrates.—If the drying is conducted over H_2SO_4 the hydrate $Bi_2O_4.H_2O$ is obtained. If $Bi_2O_5.xH_2O$ (*v. infra*) is treated with warm HNO_3Aq until the colour is orange-yellow, washed, and dried over H_2SO_4, the hydrate $Bi_2O_4.2H_2O$ is obtained. These hydrates are also formed, the first by the action of ordinary air on Bi_2O_4, and the second (with $2H_2O$) by the action of moist air on Bi_2O_4: they part with their water of hydration at about 150°.

Properties and Reactions.—Bi_2O_4 is a brownish-yellow solid; S.G. $\frac{20°}{20°}$ 5·6; deoxidised (to Bi_2O_3) and dissolved by fairly conc. HNO_3Aq, or HClAq, more slowly by conc. H_2SO_4; slightly deoxidised by contact with water in direct sunlight, oxidised to $Bi_2O_5.xH_2O$ by Cl in presence of hot conc. KOHAq; is not oxidised by ozonised O at 100°–140°; heated in Cl gives $BiCl_3$ and a little $Bi_4O_4Cl_4$; heated in Br gives $BiBr_3$ and considerable quantity of $Bi_{11}O_{15}Br_3$. Heated in CO reduction begins at abt. 105° and the change to Bi_2O_3 is complete at about 245°–250°; with H the corresponding temperatures are abt. 200° and 265°, respectively; heated in air or in O the temperatures are abt. 240° and 320°, respectively. Neither of the hydrates exhibits any decided acidic functions.

BISMUTHIC OXIDE, AND HYDRATE, Bi_2O_5 (*Bismuth peroxide*). $Bi_2O_5.H_2O$ (*Bismuthic acid*). S.G. Bi_2O_5 5·917 (Brauner a. Watts, *P.M.* 1881, 62). S.V.S. 42. S.G. $Bi_2O_5.H_2O$ 5·75.

Preparation.—Bi_2O_3, or BiO_3H_3, or BiOCl, is suspended in about 10 parts of conc. KOHAq, S.G. about 1·38, the liquid is kept nearly boiling and Cl is passed in until a dark-red homogeneous solid is formed; this solid is washed with hot water until the washings do not change the colour of red litmus paper and every trace of chloride is removed, it is then warmed for a very short time with a little conc. HNO_3Aq until its colour is scarlet, washed repeatedly and quickly with dilute HNO_3Aq, each quantity of acid being more dilute than the preceding, and then with cold water until every trace of acid is removed. If the solid is now dried over H_2SO_4, $Bi_2O_5.H_2O$ is obtained; if this is dried at 120° Bi_2O_5 remains (Pattison Muir, *C. J.* 39, 22).

Properties and Reactions.—A red, heavy powder; combines with water to form $Bi_2O_5.H_2O$; in contact with much water is slowly deoxidised with production of hydrates of Bi_2O_4 and Bi_2O_3; also deoxidised by hot dilute HNO_3Aq, giving first $Bi_2O_4.2H_2O$, and then hydrates of Bi_2O_3. Deoxidised to Bi_2O_4 by heating in current of air or oxygen at about 250°, and to Bi_2O_3 by heating in the same gases to about 305°; reduction in CO begins at about 70°, in H at about 100°; reduction to Bi_2O_4 is complete in H current at about 215°, and to Bi_2O_3 at about 255°. Reacts with Cl_2 and Br_2 to give $BiCl_3$ and a little $Bi_4O_4Cl_4$, and $BiBr_3$ and a little $Bi_{11}O_{15}Br_3$

respectively. Does not exhibit any decided acidic functions; $Bi_2O_5.H_2O$, however, dissolves in about 100 parts of boiling KOHAq so concentrated that solidification begins the moment **the lamp is removed**; on cooling, dissolving in **as little water** as possible, and nearly neutralising by HClAq (or by exposure to air) yellowish-white solids are obtained from which all potash is removed only by very long-continued washing with boiling water. The solids dried at 100° contain a little water, Bi, and generally rather more O than is required by Bi_2O_5. Solutions of $Bi_2O_5.H_2O$ in very conc. boiling KOHAq, therefore, probably contain compounds of the form $xBi_2O_5.yK_2O$. In the preparation of Bi_2O_4 the very conc. KOHAq dissolves a little of the Bi_2O_5 as this is formed; on nearly neutralising with HClAq a white pp. is obtained, which, after long-continued washing with boiling water, consists of $Bi_2O_5.3H_2O$ (Pattison Muir a. Carnegie, *C. J.* 51, 77). In the preparation of Bi_2O_5 a portion of the potash is very obstinately retained; the whole of the potash can scarcely be removed by washing with boiling water: compounds of the form $xBi_2O_5.yK_2O$ are probably formed, but every attempt to isolate these bodies has failed.

Bismuth, Oxyhaloid compounds of. Oxybromides, oxychlorides, oxyiodides, and an oxyfluoride, of bismuth have been prepared. All the haloid compounds BiX_3, where X = Cl, Br, or I, are oxidised by heating in air; only a very little BiOI is produced by long-continued heating BiI_3; $BiBr_3$ gives $Bi_8O_{11}Br_2$, as $BiCl_3$ gives $Bi_4O_5Cl_2$. The same oxyhaloid compounds are formed by the reaction between N oxides, (from starch and hot HNO_3Aq) and hot BiX_3: the oxidation is carried furthest in the case of $BiBr_3$, in this case the whole or nearly the whole of the haloid compound may be oxidised. The most stable haloid compounds towards oxidisers are BiF_3 and BiI_3.

OXYBROMIDES. Three oxybromides are known: BiOBr, $Bi_{11}O_{14}Br_5$, and $Bi_8O_{11}Br_2$.

Bismuthyl bromide, BiOBr, is produced by the action of water on $BiBr_3$; or by heating together Bi_2O_3 and $BiBr_3$; or by dissolving Bi_2O_3 in HBrAq ($BiBr_3$ is formed in solution) and adding Bi_2O_3 little by little. It is a white amorphous powder; S.G. $\frac{20°}{20°}$ 6·7; insoluble in water; unchanged when heated to redness; mixed with charcoal and heated in dry Cl, $BiCl_3$ is formed; reacts with cold HClAq to form $BiCl_3$ and $BiBr_3$, with cold HIAq to form BiI_3 and HBrAq, and with hot HFAq to form $BiBr_3$, BiOF and $BiF_3.3HF$. BiOBr heated in NH_3 is reduced to Bi, and a little $xBiBr_3.yNH_3$ is formed, x probably = 2 and y probably = 5 (Pattison Muir, *C. J.* 29, 144).

The *oxybromide* $Bi_{11}O_{15}Br_3$ is produced by heating dry Bi_2O_3 with excess of Br for some hours and removing uncombined Br by warming in free contact with air. It is a cream-coloured, non-deliquescent, amorphous powder: unchanged by heating in air; unacted on by water; dissolved by warm HClAq and HNO_3Aq (P. M., *C. J.* 31, 24).

The *oxybromide* $Bi_8O_{11}Br_2$ is produced (1) by slowly subliming $BiBr_3$ in contact with a little air; (2) by passing N oxides (obtained by heating starch and HNO_3Aq) into melted $BiBr_3$; **in the first reaction only a little of the $BiBr_3$ is oxidised, in the second reaction most of the $BiBr_3$ is oxidised. In either case the product is washed with water and dried at 100°. This oxybromide is a grey, lustrous, crystalline, powder; unchanged by water, or by heating to redness; soluble in HClAq and conc. HNO_3Aq; slowly reduced by H, finally giving Bi; heated in dry NH_3, Bi remains, and a greyish-green sublimate of $2BiBr_3.5NH_3$ is formed (P. M., *C. J.* 30, 12; 31, 24; 32, 40).

OXYCHLORIDES. Three oxychlorides, BiOCl, $Bi_2O_3Cl_2$, $Bi_4O_5Cl_2$ (or $Bi_4O_5Cl_4$), are known.

Bismuthyl chloride, BiOCl, is formed by adding water to $BiCl_3$ in a little HClAq; or by pouring $Bi.3NO_3$ in HNO_3Aq into dilute NaClAq; or by reacting on excess of Bi_2O_3 with very dilute HClAq; or by digesting a solution of $BiCl_3$ in HClAq with excess of Bi_2O_3. The pp. is washed with cold water and dried at 100°. This compound is a white, lustrous, crystalline, powder (known commercially as 'pearl white') S.G. $\frac{20°}{20°}$ 7·2. Reacts with cold HBrAq to give $BiCl_3$ and $BiBr_3$; with cold HIAq to give $BiCl_3$ and BiI_3; with hot HFAq to form $BiCl_3$, BiOF, and $BiF_3.3HF$. Reduced to $BiCl_3$ by heating with charcoal in dry Cl (Jacquelain, *J. pr.* 14, 1; Arppe, *P.* 64, 237: Oesten, *P.* 110, 128; Heintz, *P.* 63, 55; Pattison Muir, *C. J.* 39, 37).

The *oxychloride* $Bi_3O_4Cl_4$ is said to be produced by heating BiOCl to redness (Arppe).

The *oxychloride* $Bi_4O_5Cl_2$ is formed in small quantities by slowly subliming $BiCl_3$ in contact with a little air, and in large quantities by passing N oxides (by heating starch with HNO_3Aq) into melted $BiCl_3$. The analytical numbers agree fairly with $Bi_4O_5Cl_2$ and also with $Bi_4O_5Cl_4$. The compound is a yellowish-white, hard, crystalline, solid; unchanged in air, or by water or by heating to redness; soluble in hot HClAq or HNO_3Aq; boiled with NaOHAq, Bi_2O_3 and NaClAq are formed (P. M., *C. J.* 32, 40).

OXYFLUORIDE. Only one is known. *Bismuthyl fluoride*, BiOF, is obtained by heating Bi_2O_3 with large excess of HFAq so long as any reaction occurs, boiling the residue with water until every trace of acid is removed, and drying at 100°; if the washing is conducted with cold water until nearly neutral, BiOF.2HF remains; when this is strongly heated in a closed Pt crucible, BiOF is obtained in crystalline form. The liquid obtained by boiling Bi_2O_3 with HFAq evaporated at 100° gives $BiF_3.3HF$; when this salt is boiled with water it is slowly decomposed to BiOF. BiOF is a heavy, white, crystalline, powder; S.G. $\frac{20°}{20°}$ 7·55. With HF it forms the double compound BiOF.2HF. Reacts with cold HClAq to form $BiCl_3$ and HFAq; with HBrAq to form $BiBr_3$ and HFAq; with HIAq to form BiI_3 and HFAq (P. M., Hoffmeister a. Robbs, *C. J.* 39, 21).

OXYIODIDES. *Bismuthyl iodide*, BiOI, is produced by boiling BiI_3 with H_2O in small quantities, by subliming BiI_3 in air; or, also in small quantities only, by reacting with N oxides (from starch and hot HNO_3Aq) on hot BiI_3. BiOI is a heavy, red, crystalline powder, unchanged by water, or by heating in air; by long-continued heating to bright redness in air a very little Bi_2O_3 is formed; reacts with HClAq, HBrAq, and HFAq, similarly to bismuthyl chloride

and bromide (Schneider, *J. pr.* 74, 424; P. M., H. a. R., *l.c.*).

Another *oxyiodide*, probably $8BiOI.4Bi_2O_3$, is obtained as a yellow powder by pouring a dilute solution of $Bi3NO_3$ into KIAq mixed with $NaC_2H_3O_2Aq$ (Fletcher a. Cooper, *Ph.* 1882).

Bismuth, Oxysulphide of. According to Hermann (*J. pr.* 75, 452) the compound $Bi_6O_3S_4$ is formed by heating 1 part S with 6·55 parts Bi_2O_3 to low redness in a retort; S.G. 6·3. A compound of Bi, S, and O, occurs as *Karelinite* (said to be Bi_4O_3S).

Bismuth, Phosphide of. No definite compound has been isolated. Berzelius (*Lehrbuch*, 2, 582 [5th ed.]) says the two elements do not unite directly, but that a phosphide is formed by leading PH_3 into $Bi.3NO_3$ solution.

Bismuth, Salts of. These compounds are obtained in a few cases by the reaction between Bi and an acid, *e.g.* $Bi.3NO_3$, but more generally by using $Bi_2O_3.xH_2O$ in place of Bi, or by double decomposition from $Bi.3NO_3$ in HNO_3Aq or $BiCl_3$ in HClAq. Bismuth salts are insoluble in water; they are decomposed by water with production of so-called basic salts; the salts of Bi may indeed be arranged in two classes, normal and basic, as types of which may be taken the nitrates $Bi.3NO_3$ and $BiO.NO_3$, respectively. Many of these basic salts are most simply regarded as derived from acids by replacement of H by BiO; they are often called bismuthyl salts: other basic salts, however, at present at any rate, are best represented as compounds of acid-forming oxides with Bi_2O_3. All the basic nitrates for instance, and many of these salts are known, belong to the general form $xBi_2O_3.yN_2O_5.H_2O$. The salts obtained by reactions between acids and the oxides Bi_2O_4 and Bi_2O_5 are the same as those which are formed when Bi_2O_3 is used. The more important salts of Bi are the *nitrates* and *sulphates*, also *bromate*, *chlorate*, *oxalates*, *phosphates*, *tartrates*, &c. (*v.* NITRATES, SULPHATES, &c. &c.).

Bismuth, Selenide of. Bi_2Se_3. Black, lustrous, metal-like, powder; S.G. 6·82. Obtained by passing H_2Se into $Bi.3NO_3$ in as little HNO_3Aq as possible, or by heating together 1 part Se and 1·8 parts Bi, and repeatedly melting the product in contact with Se. Insoluble in solutions of alkalis or alkali-sulphides; decomposed by HNO_3Aq; gives up Se when heated. Combines with $BiCl_3$ (*v. infra*) (Berzelius; Schneider, *P.* 94, 628).

Bismuth, Selenochloride of. BiSeCl. ($=Bi_2Se_3.BiCl_3$). Formed by adding powdered Bi_2Se_3 to molten $2NH_4Cl.BiCl_3$. Steel-grey, needle-shaped, crystals. Heated in CO_2 is separated into Bi_2Se_3 and $BiCl_3$ (Schneider, *l.c.*).

Bismuth, Sulphides of. One well-marked sulphide of Bi, Bi_2S_3 is known; another, Bi_2S_2, corresponding to the oxide Bi_2O_2, probably exists. Attempts to prepare a sulphide with more S than Bi_2S_3 have failed (Pattison Muir, *C. J.* 33, 192). Sulphide of bismuth does not react with more positive sulphides as a salt-forming compound (comp. Schneider, *Z.* [2] 5, 630 with P. M., *C. J.* 33, 192).

BISMUTH TRISULPHIDE. Bi_2S_3. Occurs native as *bismuth glance*. S.G. 6·5. Rhombic forms, $a:b=1:·9881$; isomorphous with As_2S_3 and Sb_2S_3. Obtained by heating a mixture of 1 part S with 4½ parts Bi till a grey crystalline mass is formed, and then repeatedly heating this with a little S: also by passing H_2S into an acid solution of a Bi salt. If the pp. thus obtained is heated with an alkali-sulphide solution to 200° the Bi_2S_3 is said to become crystalline. Steel-grey, crystalline, lustrous, solid: strongly heated it is separated into Bi and S; unacted on by alkali or alkali-sulphide solutions.

BISMUTH DISULPHIDE. $2Bi_2S_2.H_2O$. Said to be ppd. by H_2S from alkaline solutions of Bi_2O_2. Schneider (*P.* 97, 480) dissolved 8 grams Bi tartrate in the necessary quantity of KOHAq, added air-free water to make up to 1500 c.c., then 2 grams $SnCl_2$ in KOHAq, and passed in air-free H_2S until the liquid became colourless. He washed the black pp. with KOHAq and then with H_2O (air-free), and dried at 100°. A black powder; becomes lustrous by compression; decomposed by heating into Bi and Bi_2S_3, by HClAq into Bi, $BiCl_3$, and H_2S.

Bismuth, Sulphochloride of, *v.* BISMUTH, THIO-HALOID COMPOUNDS OF.

Bismuth, Sulphoiodide of, *v.* BISMUTH, THIO-HALOID COMPOUNDS OF.

Bismuth, Sulphocyanide of, $Bi(SCN)_3$, *v.* CYANIDES.

Bismuth, Telluride of. No definite compound has been isolated; *telluric bismuth*, approximately $Bi_2S_3.2Bi_2Te_3$, occurs native. According to Berzelius (*Lehrbuch*, 2, 583 [5th ed.]) the two elements may be melted together in all proportions.

Bismuth, Thiohaloid compounds of. Only two are known: BiSCl, and BiSI. The former is obtained by the direct reaction between $BiCl_3$ and S, but BiI_3 and S do not react together; when $BiBr_3$ and S are heated together there are indications of the formation of a thio-compound, but none has yet been isolated (*v.* P.M., H. a. R., *C. J.* 39, 21). The thio-compounds are much less stable than the corresponding oxy-compounds; *v.* BISMUTH, OXYHALOID COMPOUNDS OF.

BISMUTH THIOCHLORIDE (*sulphochloride*) BiSCl. Obtained by heating S with $BiCl_3$, or by adding powdered Bi_2S_3 to molten $2NH_4Cl.BiCl_3$, and washing the product with very dilute HClAq. Small, metal-like, greyish, needles; easily decomposed into its constituents, *e.g.* by heating in CO_2, by H, by HClAq or HNO_3Aq, and by alkalis (Schneider, *P.* 93, 464).

BISMUTH THIO-IODIDE (*sulpho-iodide*), BiSI, is said to be formed, as long needles, by strongly heating I, S, and Bi_2S_3, placed in alternate layers in a large crucible (*P.* 110, 147).

Bismuthic Acid and Bismuthates (so called). $Bi_2O_5.H_2O$ is sometimes called bismuthic acid; bodies obtained by dissolving Bi_2O_5 in much molten KOH, or by saturating with Cl conc. KOHAq holding Bi_2O_3 in suspension, have been described as bismuthates. But later experiments have shown that these bodies cannot be isolated although they probably exist in presence of much potash. The acidic functions of $Bi_2O_5.H_2O$ are extremely feeble, *v.* BISMUTHIC OXIDE under BISMUTH, OXIDES OF, p. 515.

M. M. P. M.

BISMUTH, ORGANIC DERIVATIVES.

Bismuth mono-methyl compounds.

Di-chloride $BiMeCl_2$. [242°]. Obtained by adding $BiMe_3$ to an acetic acid solution of $BiCl_3$. White plates. M. sol. alcohol and acetic acid, insol. ether (Marquardt, *B.* 20, 1520).

Di-bromide $BiMeBr_2$. [214°]. Formed by mixing ethereal solutions of $BiMe_3$ and $BiBr_3$. Yellow powder. Sl. sol. alcohol, benzene, and acetic acid, insol. ether (M.).

Di-iodide $BiMeI_2$. [225°]. Formed by heating $BiMe_3$ with methyl iodide at 200° (M.). Glistening red crystals. Sol. alcohol, sl. sol. acetic acid, insol. ether.

Oxide BiMeO. Formed by adding NH_3 to an alcoholic solution of the double compound of $BiMeBr_2$ and $BiBr_3$, which is obtained as a yellow crystalline pp. on mixing ethereal solutions of $BiMe_3$ (1 mol.) and $BiBr_3$ (2 mols.) (Marquardt, *B.* 20, 1522). White powder. Insol. water. Dissolves in NaOH and in dilute HNO_3. Ignites in the air if gently warmed.

Bismuth di-methyl compounds.

Chloride $BiMe_2Cl$. [116°]. Formed by passing chlorine into a solution of $BiMe_3$ in petroleum-ether, cooled in a freezing-mixture. White micro-crystalline powder. V. sol. alcohol, insol. ether (Marquardt, *B.* 20, 1519).

Hydroxide $BiMe_2(OH)$. Formed by the action of water upon the double compound of $BiBr_3$ and $BiMe_2Br$, which is ppd. as an oily liquid by mixing ethereal solutions of equal mols. of $BiBr_3$ and $BiMe_3$. Crystalline solid. Ignites in the air spontaneously. Dissolves in aqueous NaOH. Decomposed by aqueous HCl with evolution of CH_4 (Marquardt, *B.* 20, 1523).

Bismuth tri-methide $BiMe_3$. *Tri-methyl-bismuthine.* (110°). S.G. 2·3 at 18°. Obtained by slowly adding an ethereal solution of bismuth bromide (2 mols.) to an ethereal solution of zinc methide (rather more than 3 mols.). Mobile refractive liquid, of unpleasant pungent odour. In the air it fumes and rapidly oxidises, when heated in the air it explodes violently. Volatile with steam, but decomposes on long boiling with water. Dilute H_2SO_4 or HNO_3 have little action upon it, but conc. HCl decomposes it with evolution of CH_4 and production of $BiCl_3$. It does not combine with alkyl haloids or with halogens. The latter replace Me forming $BiMe_2Cl$, &c. (Marquardt, *B.* 20, 1517).

Bismuth mono-ethyl compounds.

Chloride $BiEtCl_2$. Prepared by adding alcoholic $HgCl_2$ to alcoholic $BiEt_3$ (*q.v.*).

Iodide $BiEtI_2$. From the chloride and KI. Golden, six-sided plates.

Oxide BiEtO. From the iodide and potash. Yellow amorphous powder, takes fire in air.

Nitrate $BiEt(NO_3)_2$. From the oxide and HNO_3. Crystalline tufts.

Bismuth di-ethyl bromide $BiEt_2Br$. Formed by dropping bromine into a cooled solution of $BiEt_3$ in petroleum-ether. White powder. V. sol. alcohol, insol. ether. Ignites in the air on warming (Marquardt, *B.* 20, 1520).

Bismuth tri-ethide $BiEt_3$. *Tri-ethyl-bismuthine.* (107°) at 79 mm. S.G. 1·82.

Preparation.—1. An alloy of Bi and K is made by strongly heating bismuth (5 pts.) with cream of tartar (4 pts.). This alloy is treated with EtI (Breed, *A.* 82, 106).—2. Obtained by slowly adding an ethereal solution of bismuth bromide (2 mols.) to an ethereal solution of $ZnEt_2$ (rather more than 3 mols.) (Marquardt, *B.* 20, 1519).

Properties.—Stinking oil. It cannot be distilled at ordinary atmospheric pressure, for on heating to 150° it detonates violently; volatile with steam. Fumes and takes fire in air. V. sol. alcohol, ether, and acetic acid. Its ethereal solution exposed to air deposits $Bi_2O_3H_2O$. Forms unstable compounds with non-metals. $BiEt_2S.Bi_2S_3$ is a yellow solid, insoluble in water, soluble in yellow ammonium sulphide. $BiEt_3$ throws down calomel from alcoholic $HgCl_2$, but when alcoholic $HgCl_2$ is added to alcoholic $BiEt_3$, crystals of $BiEtCl_2$ may be got: $BiEt_3 + 2HgCl_2 = 2HgEtCl + BiEtCl_2$ (Dünhaupt, *A.* 92, 371).

Bismuth-tri-phenyl $Bi(C_6H_5)_3$. *Tri-phenyl-bismuthine.* [82°]. S.G. 1·5851 at 20°. Formed by heating bromo-benzene containing some acetic ether with an alloy of sodium and bismuth (10 p.c. Na). Colourless needles or tablets. Sol. hot alcohol, sparingly in cold, v. sol. ether and petroleum ether. By boiling with conc. HCl it is completely decomposed into benzene and bismuth chloride. It combines with Cl_2 forming the *chloride* $(C_6H_5)_3BiCl_2$ which crystallises in thick prisms, [110°], sol. hot alcohol, sl. sol. ether and cold alcohol, v. sol. benzene, not decomposed by conc. HCl. The *bromide* $(C_6H_5)_3BiBr_2$ forms long prisms, [119°], v. sol. benzene, sl. sol. alcohol and ether (Michaelis a. Weitz, *B.* 20, 51).

BITTER ALMOND OIL *v.* ALMONDS and BENZOIC ALDEHYDE.

BIURET $C_2H_5N_3O_2$ *i.e.* $NH_2.CO.NH.CO.NH_2$. *Allophanamide.* Mol. w. 103. [190°]. S. 1·25 at 0°; 1·51 at 15°; 15 at 105°.

Formation.—1. Urea is heated at 150°–170° until the melted mass becomes pasty and ceases to give off NH_3. The product is extracted with hot water (Wiedemann, *P.* 74, 67; Hofmann, *B.* 4, 262).—2. By passing the vapour of cyanic acid into melted urea (Finck, *A.* 124, 331).—3. Urea is treated with chlorine till the mass becomes pasty (Hoppert a. Bögel, *Z.* [2] 3, 691; *B.* 4, 175). 4. By the action of NH_3 on allophanic ether (H. a. B.). 5. By heating 'amido-di-cyanic acid' (p. 163) with H_2SO_4 (1 pt.) and water (2 pts.) at 60°–70° (Baumann, *B.* 8, 708).—6. By the action of NH_3 aq on tri-bromo-acetyl-urea (Baeyer, *A.* 130, 154). 7. By heating urea with PCl_3 at 100° (Weith, *B.* 10, 1743). 8. By mixing dilute solutions of urea and potassic cyanate, acidifying with acetic acid, evaporating, adding a little H_2SO_4 and extracting with alcohol (Drechsel, *J. pr.* 128, 472). 9. By electrolysis of a solution of NH_3, using carbon electrodes (Millot, *Bl.* [2] 46, 244).

Properties.—Long needles (containing aq); or long anhydrous laminæ (from alcohol). Split up by heat into NH_3 and cyanuric acid. Dissolves unchanged in cold conc. H_2SO_4. Its solution is not ppd. by salts of lead or silver or by tannin. A little $CuSO_4$ followed by KOH gives a deep violet solution.

Reactions.—1. At 120° it absorbs HCl forming B'_2HCl which at 160°–170° in a current of HCl gives H_2O, CO, guanidine, cyanuric acid, and urea.—2. Boiling conc. HClAq forms NH_3, urea, and guanidine.—3. Boiling *baryta-water*

forms CO_2, NH_3, and urea.—4. With NaClO it evolves $\frac{1}{3}$ of its nitrogen, with NaBrO it evolves $\frac{2}{3}$ (Fenton, *C. J.* 35, 14).—5. HNO_3 gives CO_2 and N_2O in equal volumes (Franchimont, *R. T. C.* 6, 216).—6. $COCl_2$ at 60° forms **carbonyl-di-biuret** $(C_2H_4N_3O_2)_2CO$ (E. Schmidt, *J. pr.* [2] 5, 47); a crystalline powder, v. sl. sol. cold water, insol. alcohol and ether. This body is converted by boiling baryta-water into urea and cyanuric acid; and by $COCl_2$ at 140° into cyanuric acid; $Hg(NO_3)_2$ gives, in hot dilute solution, a pp. of $C_3H_8N_6O_5 3HgO$.

Salts.—B'_2HCl; decomposed by water.—$Ag_2C_2H_3N_3O_2$: ppd. by adding $AgNO_3$ (2 mols.) and NH_3Aq to a saturated aqueous solution of biuret (1 mol.); sol. HNO_3 and NH_3Aq (Bonné a. Goldenberg, *B.* 7, 287).—**Cyanurate** $B'C_3N_3H_3O_3$: needles; formed on crystallising biuret from water. It has probably been mistaken for urea cyanurate from which it differs in yielding with baryta water, barium cyanurate and biuret, in giving off 3 atoms of nitrogen as ammonia when heated with barium hydrate (urea cyanurate yields 2 atoms), in giving off 14·8 p.c. nitrogen with sodium hypobromite, (while urea cyanurate gives 11·5 p.c., both results corresponding to 2 atoms nitrogen) (Herzig, *M.* 2, 111).

Biuret dicyanamide $C_4H_9N_7O_2$ *i.e.* $NH(CO.NH.C(NH).NH_2)_2$. From acetyl-urea (2 pts.) and guanidine carbonate (5 pts.) at 110°–150° (Rasinski, *J. pr.* [2] 27, 157). Amorphous substance, v. sol. acids and fixed alkalis, insol. NH_3Aq. Does not give the biuret reaction with $CuSO_4$.

BIXIN $C_{28}H_{34}O_5$. [176°]. A colouring matter contained in annatto seeds (*Bixa orellana*) (Preisser, *A.* 52, 382; Girardin, *J. Ph.* [3] 21, 174; Bolley a. Mylius, *Bl.* [2] 3, 230; Stein, *J. pr.* 102, 175).

Preparation.—Annatto (1,500 g.) is digested at 80° with alcohol (2,500 g. of 80 p.c.) with addition of Na_2CO_3 (150 g.); after filtration, the residue is again digested with alcohol (1,500 g. of 60 p.c.). The mixed filtrates are ppd. by adding half their bulk of water and conc. Na_2CO_3Aq; the ppd. sodium-bixin is dissolved in alcohol (60 p.c.) and re-ppd. with Na_2CO_3Aq. The sodium-bixin is then decomposed by HCl (Etti, *B.* 11, 864; 7, 446).

Properties. Minute red leaflets; insol. water, sl. sol. alcohol, benzene, CS_2, and acetic acid, v. e. sol. ether. Conc. H_2SO_4 forms a bright blue solution, whence water gives a dark green pp. It reduces cold Fehling's solution.

Reactions.—1. Distillation with zinc dust gives *m*-xylene, ethyl-toluene, and an oil $C_{14}H_{14}$ (270°–280°). Reduced by sodium-amalgam to $C_{28}H_{40}O$.

Salts. $C_{28}H_{33}NaO_5 2aq$: lustrous red crystals, v. sol. water, insol. alcohol, and ether. — $C_{28}H_{32}Na_2O_5 2aq$: dull red powder. — $C_{28}H_{33}KO_5 2aq$. $C_{28}H_{32}K_2O_5 2aq$.

BLEACHING-POWDER *v.* HYPOCHLORITES, under CHLORINE, OXYACIDS OF.

BLOOD. In vertebrates, the blood is a somewhat viscous, and to the naked eye homogeneous, red liquid. The blood which leaves the lungs or gills is of a bright scarlet colour, and that in the systemic veins of a purplish hue, which on exposure to the air, or on shaking with oxygen, becomes of the bright arterial scarlet colour. This difference in tint is due to the amount of oxygen present in combination with the red pigment hæmoglobin; in the lungs a loose combination called oxy-hæmoglobin is formed which is scarlet; in the tissues this oxygen is given up, and the blood returning to the heart is of the purplish colour due to hæmoglobin.

Specific Gravity. Roy (*Proc. Physiol. Soc.* 1884) has introduced a method for ascertaining the specific gravity of living blood. A drop of blood is introduced into a mixture of glycerin and water of known specific gravity; if the drop tends to rise or sink, it is assumed that it is of lower or higher specific gravity than the liquid in which it is placed. The average specific gravity of human blood thus found was 1·060. Defibrinated human blood has an average specific gravity of 1·055. Pflüger (*Pflüger's Archiv*, i. 75) found the specific gravity of dog's blood to be 1·060; and Gschleidlen that of rabbit's blood 1·048.

Characters.—Blood is always feebly alkaline in reaction (Kühne, *Virchow's Archiv*, 33, 65; Liebreich, *B.* 1, 48; Schäfer, *Journal of Physiology*, 3, 292). Under the microscope the blood is seen not to be a homogeneous red liquid, but to consist of a nearly colourless liquid, the plasma or liquor sanguinis, holding in suspension large numbers of solid bodies, the corpuscles. These corpuscles are of two kinds, the coloured and the colourless.

Red corpuscles. These owe their colour to hæmoglobin, and are much more numerous than the white corpuscles. They vary in size and structure in different groups of the vertebrate sub-kingdom. In Mammalia, with the exception of the Camelidæ, they are biconcave, circular discs; they have no nucleus except during embryonic life; and they have a tendency to run into rouleaux when the blood is at rest, but if it is disturbed they readily become separated. In the Camel tribe they have an elliptical outline. Their average diameter in mammals is ·007–·008 millimetre and about one-fourth of that in thickness; there are very slight variations in different classes of mammals. In birds, reptiles, amphibians, and fishes, the red corpuscles are biconvex, oval discs, with a nucleus; they are largest in the amphibia. C. Schmidt gives the specific gravity of red blood corpuscles as 1·089, Welcker as 1·105.

According to C. Schmidt, 1,000 parts of moist red corpuscles contain—

Water		688 parts.
Solids	Organic	303·88 „
	Mineral	8·12 „

According to Hoppe Seyler and Jüdell (*Med. Chem. Untersuchungen*, Heft iii. p. 386) 100 parts of dried corpuscles contain—

	Human blood I.	Human blood II.	Dog's blood	Goose's blood
Proteids	12·24	5·10	12·55	36·41
Hæmoglobin	86·79	94·30	86·50	62·65
Lecithin	0·72	0·35	0·59	0·46
Cholesterin	0·25	0·25	0·36	0·48

The nuclei of the red corpuscles consist mainly, according to Lauder Brunton, of nuclein, a substance very akin in its properties to mucin (*Journal of Anat. and Physiology*, 2nd series,

vol. 8, p. 91). The mineral constituents of the red corpuscles have been investigated by C. Schmidt, and the following tables contrast those of the red corpuscles with those of the plasma in man.

1000 parts of moist corpuscles yield—

Mineral matter (exclusive of iron, which is contained in the hæmoglobin	8·120
Chlorine	1·686
Sulphuric anhydride	0·066
Phosphorus pentoxide	1·131
Potassium	3·328
Sodium	1·052
Calcium phosphate	0·114
Magnesium phosphate	0·073

1000 parts of plasma yield—

Mineral matter	8·550
Chlorine	3·640
Sulphuric anhydride	0·115
Phosphorus pentoxide	0·191
Potassium	0·323
Sodium	3·341
Calcium phosphate	0·311
Magnesium phosphate	0·222

The remarkable difference in the distribution of potassium and sodium seen in the above does not, however, hold for most animals as the following table shows (Gamgee, *Physiological Chemistry*, p. 122).

Blood Cells.

	K.	Na.	Cl.
Man	40·89	9·71	21·00
Dog	6·07	36·17	21·88
Cat	7·85	35·02	27·59
Sheep	14·57	38·07	27·21
Goat	37·41	14·98	31·73

Liquor Sanguinis.

	K.	Na.	Cl.
Man	5·19	37·74	40·68
Dog	3·25	39·68	37·31
Cat	5·17	37·64	41·70
Sheep	6·56	38·56	40·89
Goat	3·55	37·89	40·11

Probably the only gaseous constituent of the red blood corpuscles not in a state of chemical combination is carbonic acid.

Blood tablets. Besides the red corpuscles, a number of colourless discs of ·002-·003 millimetre diameter are also seen: they are also called hæmatoblasts (*Blutplättchen* of Bizzozero). By some they are supposed to be stages in the development of red corpuscles; by others to take part in the formation of fibrin. Wooldridge considers them to be identical with the proteid he calls fibrinogen A, which can be precipitated from liquor sanguinis by exposure to cold.

Colourless corpuscles or leucocytes. These are animal cells, and consist of nucleated masses of protoplasm, more or less granular, and exhibiting during life contractility, the movements so produced being called amœboid. They are not constant in size, but in man they average about 0·01 millimetre; they are somewhat larger in the lower vertebrate groups. In mammals there is on the average one white or colourless corpuscle to 330 or 350 red ones.

Our knowledge of the chemical constituents of the white corpuscles is meagre; they are lighter than the red ones; the great mass of the protoplasm is undoubtedly proteid in nature; and the nucleus consists mainly of nuclein (Miescher, *Med. Chem. Untersuch.*, Heft iv., p. 441). By micro-chemical investigation, the presence of glycogen can often be demonstrated by iodine, and of fat granules by osmic acid.

Coagulation of blood. Within a few minutes after having been shed, blood passes first into the state of a soft red jelly, which gradually acquires greater consistence; and by the contraction of one of its constituents expresses a fluid, the serum, in which the clot or *crassamentum* ultimately floats.

Coagulation is due to the separation from the blood plasma of a solid proteid substance called fibrin. The clot consists of fibrin entangling the corpuscles. By stirring blood, or whipping it with twigs immediately after it is shed, fibrin free from corpuscles adheres to the twigs as a yellowish stringy mass. Under the microscope, coagulation is seen to consist of the separation of fine filaments from the plasma, which start from or entangle the blood plates, and corpuscles.

Coagulation of the blood is hastened by exposure to a temperature rather above that of the body; by contact with foreign matter, or by agitation; and by dilution with not more than twice its volume of water. Coagulation is hindered or prevented by exposure to a low temperature; by contact with living tissues, or by the addition of large quantities of neutral salts such as sodium chloride, sodium sulphate, or magnesium sulphate. When these precautions are taken, the corpuscles sink, and the plasma can be drawn off: in the last case mixed however with salt solution, the inhibitory influence of which on coagulation can be removed by diluting the mixture with water; fibrin is then formed.

Many theories have been held with regard to the cause of the coagulation of the blood. Nearly up to the end of the last century, the clot was believed to be simply a mass of adherent corpuscles. Hewson, 1772 (v. Hewson's works, edited by Gulliver, *Sydenham Soc.*), was the first to show that it was really due to the separation of some substance from the plasma. Buchanan (*London Medical Gazette*, vol. 18) showed that squeezed blood-clot had the power of hastening the coagulation of the liquor pericardii; and as this power was especially shown by the buffy coat, he supposed that it was due to the white corpuscles; he compared the action of these corpuscles to that of rennet on milk. Denis (*Mémoire sur le sang*, 1859, p. 32), by saturating the liquor sanguinis with sodium chloride, obtained a proteid pp., which after being redissolved in water underwent coagulation. To this precursor of fibrin he gave the name *plasmine*. A. Schmidt (*Archiv f. Anat. u. Physiol.* 1861, 545) separated plasmine into its two constituents, both proteids of the globulin class, to which he gave the names fibrinogen and fibrinoplastin or paraglobulin (now called serum globulin). He thought both of these substances were necessary for coagulation, and that they united to form fibrin under the influence of a ferment. This *fibrin-ferment* he prepared from serum, by ppg. it with the serum proteids by means of absolute alcohol; after leaving the pp. some months under alcohol, the proteids were by this means rendered insoluble, while the ferment could be extracted with water.

Gamgee (*Journal of Physiology*, 1879) obtained fibrin-ferment by extracting blood-clot with 8 p.c. sodium chloride solution. The extract contained a small quantity of a globulin-like proteid, and had very marked power in inducing coagulation. Hammarsten (*Pflüger's Archiv*, 14, 211; 17, 413; 18, 38; 19, 563) modified Schmidt's theory by showing that paraglobulin is not necessary for the formation of fibrin, but that fibrinogen is the only true fibrin precursor which under the influence of the fibrin ferment is converted into fibrin. The presence of paraglobulin, however, hastens coagulation perhaps by its combining with alkaline carbonates which otherwise would impede the action of the ferment: other proteids such as casein, or even salts such as calcium chloride, will, however, take its place.

The source of the fibrin-ferment seems to be the white corpuscles. Rauschenbach has pointed out (*Ueber die Wechselwirkungen zwischen Protoplasma und Blutplasma*, Inaug. Diss. Dorpat, 1883) that leucocytes are of two kinds: *α* leucocytes which are acted upon and disintegrated by the plasma when the blood is shed, two of the products of such action being paraglobulin and fibrin ferment; and *β* leucocytes which remain unaltered.

The latest theory of the coagulation of the blood is that of L. C. Wooldridge (*Beiträge zur Physiologie*, Leipzig, 1887, 221). He injects peptone into the circulation of an animal, and kills it by bleeding; the blood remains uncoagulated for many hours, and the corpuscles are removed by centrifugalising; if a substance containing lecithin be then added to the peptone plasma, coagulation occurs. By cooling peptone plasma, a pp. is produced; this consists of little rounded discs similar to blood tablets; this is called fibrinogen A; after its removal from the plasma coagulation does not occur; the formation of fibrin is supposed to be due to the lecithin contained in fibrinogen A combining with fibrinogen B (Hammarsten and Schmidt's fibrinogen).

Human blood yields from 2·2 to 2·8 parts of fibrin per 1,000.

Serum. This is the plasma, *minus* the elements of fibrin. It contains three classes of constituents; proteids, extractives, and salts. The proteids consist of globulin and albumin. Owing to the disintegration of the white corpuscles the globulin is rather more abundant than in the plasma. The following table of Hammarsten's (*Pflüger's Archiv*, 1878) represents the percentage of these substances in the serum of some of the commoner mammals:

	Total Solids	Total Proteids	Serum Globulin	Serum Albumin
Serum from Horse	8·597	7·257	4·565	2·677
" " Ox	8·965	7·499	4·170	3·329
" " Man	9·207	7·619	3·103	4·516
" " Rabbit	7·525	6·225	1·788	4·436

The globulin appears to be a single substance; it is coagulated by heat at 75° C.: by fractional heat-coagulation, however, the serum albumin can be differentiated in some animals into two, in some into three proteids (Halliburton, *Journal of Physiology*, 5, 152; Kauder, *Arch. f. exp. Path. u. Pharmac.*, 20, 411); in the cold-blooded animals the total quantity of proteids in the serum is much lower, the serum globulin is always greatly in excess of the serum albumin, and the latter substance is not differentiable into several proteids by fractional heat-coagulation (Halliburton, *Journal of Physiology*, 8, 319).

The extractives of serum are organic substances present in small quantities, which are extracted by various liquids, especially by alcohol or ether. There is about 0·2 p.c. of fats and cholesterin; about ·08 to 0·12 p.c. of glucose (Pavy, *Croonian Lectures on Diabetes*, London, 1878); urea 0·02 to 0·04 p.c.; and creatine, creatinine, xanthine, hypoxanthine, uric acid, and hippuric acid in still smaller quantities. A yellow pigment is found dissolved in varying quantities in the serum of most animals; Hammarsten (*Maly's Jahrbericht*, 1878, 129), MacMunn (*Pr.* 31, 231) and others have described this as a biliary pigment; Krukenberg (*Sitzungsb. der Jenaischen Gesellsch. f. Med.*, 1885), and Halliburton (*Journ. of Physiology*, 8, 324) have described it as a lipochrome.

The salts of serum amount to 0·7 to 0·9 p.c.

Gases of the blood. From the blood as a whole, or from the plasma, coloured corpuscles, or serum, a mixture of carbonic acid, oxygen and nitrogen can be separated. Oxygen is present in much larger quantities than could be held in simple solution in the blood, and is, in fact, held in feeble combination with hæmoglobin; only a small part being in solution in the liquor sanguinis. Carbon dioxide is partly in a state of chemical combination, but chiefly in a state of simple solution. It is contained in great part in the liquor sanguinis, but in part also in the corpuscles. The nitrogen is held in simple solution in the liquor sanguinis. Arterial blood of the dog yields for every 100 volumes 58·3 vols. of mixed gases composed of 22·2 vols. of oxygen, 34·3 vols. of carbonic anhydride, and 1·8 vols. of nitrogen. The maximum amount of oxygen observed has been 25·4 vols. (Pflüger, *Centralbl. f. d. med. Wissensch.* 1868). In venous blood, the nitrogen is the same as in arterial, the oxygen is less in amount (from 8 to 12 vols. per 100 of blood), and the CO_2 greater (from 40–50 vols. per 100 of blood).

Lymph. This is the name applied to that portion of the blood that transudes through the walls of the blood-vessels, and after supplying the tissues with nutritive materials and receiving the products of their combustion returns to the large veins by means of the lymphatic vessels.

Lymph is a transparent liquid, which during digestion is more or less milky, owing to the suspension in it of fatty matters absorbed from the alimentary canal. Its specific gravity varies between 1·012 and 1·022, and its reaction is alkaline.

Under the microscope, the lymph is seen to contain colourless corpuscles. In a time varying from 3 to 20 minutes after it has left the vessels, lymph undergoes coagulation, fibrin being formed. The amount of fibrin which separates is between 0·4 and 0·8 per 1000, being less than that which separates from blood. Lymph is, in fact, simply dilute blood plasma; urea and carbonic acid, however, are rather more abundant in lymph than in blood.

The Blood in Disease.

Anæmia. The chief change is a reduction in the number of red corpuscles, and the diminution of the amount of hæmoglobin they contain. In severe cases there is also a reduction in the solid constituents of the plasma.

Leucocythæmia. This is associated with great increase in the number of white corpuscles, which may become nearly as numerous as the red. The blood is poor in hæmoglobin, and rich in hypoxanthine and lactic acid (Scherer). Charcot found in the blood, spleen, and liver of patients suffering from leucocythæmia colourless elongated crystals, which he and Vulpian were inclined to consider as proteid in nature; while they were regarded by Salkowski as consisting of a mucin-like substance. Schreiner states that they consist of the phosphate of a base, to the hydrochloride of which he gives the formula $C_2H_5N.HCl$ (*A.* 194, 68).

Gout. In this disease uric acid accumulates in the blood, probably owing to non-elimination by the urine; there is also a large quantity of oxalic acid (Garrod, *Medico-Chirurg. Trans.*, 31, 83; 37, 51).

Rheumatism. The fibrin is much increased in amount: the same is, however, true for other inflammatory conditions. There is no excess of uric acid in the blood. Lactic acid is said to be the *materies morbi* by some, but this has never been satisfactorily demonstrated.

Fevers.—In various zymotic fevers, and septic diseases, the presence of different forms of bacteria has been described, or in some cases only presumed to exist in the blood. The best known of these are the spirillum of relapsing fever, the bacillus anthracis of splenic fever, and the bacillus malariæ of Klebs and Crudeli of intermittent fever. Pigment granules of a dark colour are also said to occur in the blood of ague patients. It is probably a derivative of hæmoglobin (Marchiafava).

Diseases of the liver. In jaundice, bilirubin and in some cases the bile salts also accumulate in the blood; in acute yellow atrophy the blood contains leucine and tyrosine.

Diabetes mellitus. In this disease the most marked feature is an increase in the amount of glucose in the blood. The peculiar odour of the breath in diabetics is stated to be due to acetone, and death is often said to result from acetonæmia. It is probable that acetone does not exist free in the blood, but is derived from the splitting up of aceto-acetic ether.

In some cases of diabetes a lipæmic (fat in the blood) condition has been described. But there is no doubt that this may occur without evidence of disease, and also in other diseases than diabetes.

Bright's disease. In addition to an anæmic condition, there is an increase in the amount of urea in the blood. The convulsions and coma that are apt to supervene when the elimination of urea is defective have been designated evidences of uræmic poisoning. It is probable, however, that in these cases it is not urea itself which is the poison, but probably some substance or substances antecedent to urea. Frerichs' theory that the poison is ammonium carbonate is now given up as untenable.

The Blood of Invertebrate Animals.

Our knowledge concerning the blood of invertebrate animals is much less complete than that of the vertebrates. In certain marine animals the circulating fluid is chiefly sea water in which a number of corpuscles are suspended (*e.g.* echinoderms): in other invertebrates such as crustacea the blood is a highly organised fluid, and rich in proteid constituents, but even in these the amount of saline matters varies with the habitat, being much more abundant in marine than in fresh-water animals. There is never any distinction into blood proper and lymph in invertebrate animals; hence the name *hæmolymph* is sometimes given to their circulating fluid; the term *hydrolymph* is applied in those cases in which the blood is chiefly water, and contains but few organic constituents.

Hæmoglobin is contained in the blood of many invertebrates (Lankester, *Pflüger's Archiv*, 4, 315), chiefly worms, but also in a few crustaceans, insects, molluscs, leeches, and echinoderms. With the exception of four worms and two molluscs, however, it does not occur in special corpuscles as in the blood of vertebrates, but dissolved in the liquor sanguinis, colourless corpuscles only being found in the blood. In other invertebrates this red pigment is replaced by others, which apparently have a similar respiratory function; the most important of these other respiratory proteids are (1) hæmocyanin, a blue pigment occurring in various crustaceans, arachnids, and molluscs (Fredericq, *C. R.* 87, 996). This contains copper as one of its constituent elements; when oxidised it is blue, when reduced it is colourless. (2) Chlorocruorin, a green pigment, closely related to hæmoglobin, found in the blood of certain worms (Lankester, *Journ. of Anat. and Physiol.*, 2, 114). (3) Hæmerythrin, a purplish red pigment found in a few gephyrean worms (Krukenberg, *Vergl. phys. Studien*, 1ste Reihe, 3te Abth. p. 82). In all these cases, the pigment is dissolved in the blood plasma, which has thus a respiratory in addition to a nutritive function. In addition to these pigments, others occur which have apparently no respiratory function; thus chlorophyll appears in the blood plasma of many moths and butterflies (Poulton, *Pr.* 38, 269; tetronerythrin, a red lipochrome in the blood plasma of certain crustacea (Halliburton, *Journ. of Physiol.*, 6, 300). Various coloured granules are described in the corpuscles of holothurians and sea urchins (Geddes, *v.* Gamgee's *Physiol. Chem.*, 134), and the blood of the limpet is described by Krukenberg as being of an orange colour.

The blood of most invertebrates is alkaline in reaction, the only known exception being that of moths and butterflies which is acid (Poulton).

With regard to the coagulation in the blood of invertebrates Halliburton (*Journ. of Physiol.*, 6, 300) was able, in the case of the crustacea, to separate crustacean fibrin, and to show that as in vertebrate blood it was formed from a previously soluble fibrinogen under the influence of a ferment. Crustacean fibrinogen and fibrin differ but little from that of vertebrate blood and the fibrin ferment is identical with that

obtained by Schmidt from vertebrate blood. The coagulation of crustacean blood is also hindered by cold, or admixture with neutral salts. The coagulum formed when the blood of cephalopods is shed is stated by Fredericq to be only a plasmodium of cells.

[The foregoing article has only discussed blood from a general point of view. The various constituents will be described under their proper headings; the proteids including hæmoglobin and the other blood pigments will be described under the heading *Proteids*.] W. D. H.

BLOWPIPE *v.* ANALYSIS.

BOHEIC ACID $C_7H_{10}O_6$. [100°]. Occurs (to the extent of ·2 p.c.), together with quercitannic acid, in black tea (*Thea bohea*) (Rochleder, *A.* 63, 202). Yellow amorphous resin, v. sol. water and alcohol; ppd. by alcoholic or ammoniacal lead acetate.—BaA″aq.—PbA″aq.—PbA″PbO.

BOILING-POINTS *v.* PHYSICAL METHODS; sec. THERMAL.

BOLDIN $C_{30}H_{52}O_8$. A glucoside which may be extracted by boiling alcohol from the leaves of *Boldoa fragrans*, in which it occurs to the extent of ·3 p.c. It is a syrup, volatile with steam, and decomposed by hot dilute HCl into glucose, MeCl, and an oil $C_{18}H_{24}O_3$ (?) sol. alcohol, insol. water (Chapoteaut, *C. R.* 98, 1052). According to Bourgoin a. Verne (*Bl.* [2] 18, 481) the leaves of *Boldoa* contain an alkaloid, *boldine*.

BOLETUS *v.* AGARICUS.

BONE OIL (Anderson, *Tr. E.* 16, 4; 20, ii. 247; 21, i. 219; 21, iv. 571; *A.* 70, 32; 80, 44; 94, 358; 105, 335). The following substances have been isolated from the tar obtained in the dry-distillation of bones:

Chief Constituents.	*By-products.*
Butyronitrile	Methylamine
Valeronitrile	Aniline
Hexonitrile	Pyridine
Isohexonitrile	Methyl-pyridine
Deconitrile	Di-methyl-pyridine
Palmitonitrile	Quinoline
Stearonitrile	Phenol
Pyrrol	Propionitrile
Methylpyrrol	Valeramide
Dimethylpyrrol	Toluene
Hydrocarbons:	Ethyl benzene
C_9H_{14} (Dihydro-m-ethyl-toluene ?)	Naphthalene
$C_{10}H_{16}$ (Dihydro-m-methyl-cumene ?)	
$C_{11}H_{18}$	

Weidel a. Ciamician (*B.* 13, 65) consider that the nitriles are formed by the action of NH_3 at the high temperature on the fatty acids contained in the bones; the pyridine bases they believe to be formed by the combination of the acrolein (from the glycerin in the fats) with ammonia, methylamine, &c., whilst pyrrol and its homologues are products of the decomposition of gelatin.

BORATES. Salts of boric acid *v.* BORON, OXYACIDS OF, p. 528.

BORAX *v.* *Borate of sodium*: under BORON, OXYACIDS OF, p. 529.

BORIC ACID *v.* BORON, OXYACIDS OF, p. 528.

BORIC ANHYDRIDE *v.* BORON, OXIDE OF, p. 527.

BORIDES. *Compounds of boron with one other more positive element.*—Very few of these compounds exist; manganese forms a crystalline boride probably Mn_3B_2; platinum easily combines with boron to form PtB (?); and aluminium and boron appear to form a kind of alloy, the proportion of the elements in which varies within very wide limits: two definite borides of Al are also known (*v.* IRIDIUM, IRON, MANGANESE, PALLADIUM, PLATINUM, ALUMINIUM, BORIDES OF).

BORNEENE. A mixture of terpenes (*q. v.*), exuding from *Dryobalanops camphora*, holding borneol in solution (Gerhardt, *Traité*, 3, 628, 641).

BORNEOL $C_{10}H_{18}O$ *i.e.* $C_{10}H_{17}.OH$. *Borneo camphor, Tetra-hydride of* (1, 4, 6)-*methyl-propyl-phenol* (?). Mol. w. 154. [198°] (P.); [207°] (W.) (212°). R ∞ 75·30 in a 22·5 p.c. alcoholic solution (Kanonnikoff).

Occurrence.—In *Dryobalanops camphora*, being extracted from hollow cavities in the trunk of old trees (Pelouze, *A.* 40, 326). In the essential oil of valerian (Gerhardt, *A.* 45, 34; Bruylants, *B.* 11, 451). To the extent of 4 or 5 p.c. in oil of rosemary (Bruylants, *J.* 1879, 944; Weber, *A.* 238, 89).

Formation.—1. By heating camphor with alcoholic KOH (Berthelot, *A. Ch.* [3] 56, 78).—2. By the action of sodium on camphor (Baubigny, *Z.* [2] 3, 71; Haller, *C. R.* 105, 227).

Preparation from camphor.—(Jackson a. Menke, *Am.* 5, 270; 6, 404; Kachler a. Spitzer, *M.* 5, 50; *B.* 15, 16, 2730; Immendorff, *B.* 17, 1036). Camphor (50g.) is dissolved in alcohol (500 c.c. of 96 p.c.), and sodium (60g.) added slowly. Towards the end of the operation water (50 c.c.) is added (O. Wallach, *A.* 230, 225).

Properties.—Regular crystals; very readily sublimes in plates. Smells like camphor, but more peppery. Has a burning taste. The alcoholic solution is dextrorotatory; artificial borneol has a somewhat higher rotatory power (c. 43°) than the natural borneol ($[\alpha]_D = 33°$, (Biot; Kachler). V. sl. sol. water, sol. alcohol and ether. Lighter than water. The rate of etherification of borneol resembles that of primary alcohols (Menschutkin, *J. R.* 13, 162).

Reactions.—1. P_2O_5 converts it into one or more terpenes (borneene).—2. Boiling HNO_3 (S.G. 1·42) gives camphor and its oxidation products.—3. Behaves as an alcohol with regard to PCl_5.—4. HClO converts it into camphor.

Sodium borneol $C_{10}H_{17}ONa$: six-sided plates (from benzene). Combines with CO_2, forming $C_{10}H_{17}O(CO_2Na)$ (Kachler a. Spitzer, *M.* 2, 235).

Bromide.—Bromine added to an ethereal solution of borneol forms crystals of a mixture of bromides (? $C_{10}H_{18}OBr_2$ and $(C_{10}H_{18}O)_2Br_2$).

Hydrobromide. $(C_{10}H_{18}O)_2HBr$. Crystalline pp. got by passing HBr into a solution of borneol in light petroleum. The compound is unstable and is decomposed both by water and by alcohol.

Hydriodide. $(C_{10}H_{18}O)_2HI$. Prepared similarly.

Methyl derivative $C_{10}H_{17}OMe$. (194° cor.). From sodium-borneol and MeI (Baubigny, *Z.* 1868, 299).

Ethyl derivative $C_{10}H_{17}OEt$ (202°) (B.).

Formyl derivative $C_{10}H_{17}O.CHO$. (225°–230°). In oil of valerian (Bruylants).

Acetyl derivative $C_{10}H_{17}OAc$. (221°) (K. a. S.); (227°) (M.). Occurs in oil of valerian (Bruylants, *B.* 11, 456); and may be formed by the action of Ac_2O upon borneol (Montgolfier, *A. Ch.* [5] 14, 50), or of AgOAc upon bornyl chloride (Kachler a. Spitzer, *A.* 200, 352). On standing it becomes crystalline [24°]. Fusion with NaOH gives NaOAc and borneol.

Isovaleryl derivative $C_{10}H_{17}O(C_5H_9O)$. (255°–260°).

Stearyl derivative $C_{10}H_{17}O(C_{18}H_{35}O)$. From borneol and stearic acid at 200° (Berthelot, *A.* 112, 366). Oil.

Benzoyl derivative $C_{10}H_{17}OBz$. Oil.

Lævorotatory borneol $C_{10}H_{17}OH$. [35°]. (210°). (Perrot, *A.* 105, 67). $[\alpha]_D = -33°$. Occurs in the alcohol produced by fermentation of the sugar of madder-root (Jeanjean, *A.* 101, 95). Small regular crystals; sl. sol. water, rotating upon it. HNO_3 forms lævorotatory camphor.

Lævorotatory borneol $C_{10}H_{17}OH$. [204°]. S.G. 1·02. From Ngai camphor (Hanbury, *J.* 1874, 537).

Lævorotatory borneol $C_{10}H_{17}OH$. [201°]. $[\alpha]_D = -37° 21'$ in alcohol of 82 p.c. at 22°. From thymene picrate and boiling NaOHAq (Lextreit, *J. Ph.* [5] 13, 265). HNO_3 converts it into a lævorotatory camphor [176°] (204°).

Lævorotatory borneol $C_{10}H_{17}OH$. Formed, together with ordinary borneol, by the action of Na on dextro- or lævorotatory camphor (Montgolfier, *A. Ch.* [5] 14, 21; *C. R.* 89, 101).

Inactive borneol $C_{10}H_{18}O$. [199°]. (210°). Among the products of the distillation of colophene (*q. v.*). Also from its acetyl derivative. *Properties.* — Differs from dextrorotatory borneol only in being inactive. The crystals float on water, but when pressed into a solid cake they sink (unlike camphor). Oxidised by HNO_3 to inactive camphor (Armstrong a. Tilden, *C. J.* 35, 752). Heated with a large quantity of HCl it forms $C_{10}H_{16}HCl$.

Acetyl derivative $C_{10}H_{17}OAc$. (215°). From terebene and HOAc at 100° (Bouchardat a. Lafont, *Bl.* [2] 45, 164; *C. R.* 102, 171).

According to Haller there are two true borneols $[\alpha]_j = +$ or $-37°$, and the others are molecular compounds of these (*v.* CAMPHOR and CINEOL).

BORNYLAMINE $C_{10}H_{19}N$ probably $C_8H_{14}\left\langle\begin{matrix}CH_2\\ |\\ CH.NH_2\end{matrix}\right.$ [160°]. (200°). V.D. 5·5 (for 5·3). $\alpha_D = -18° 35' 41''$.

Formation.—1. By reduction of camphoroxim in alcoholic solution by means of sodium. 2. By saponification of its formyl derivative obtained by heating camphor with ammonium formate at 220°–240°.

Properties.—Crystalline solid, having an odour resembling both camphor and piperidine. In its physical properties it greatly resembles camphor. Very volatile with steam. Sublimable even at the ordinary temperature. V. sol. alcohol, ether, &c., nearly insol. water. Alkaline reaction to litmus. Takes up CO_2 from the air. Primary base. Gives the carbamine reaction. Lævorotatory. Isomeric with camphylamine.

Salts.—B'HCl: easily soluble white needles [c. 280°].—$B'_2Cl_2H_2PtCl_4$: golden-yellow plates, v. sol. hot water or alcohol.—$B'H_2SO_4$: easily soluble rhombic tables.—$B'_2H_2Cl_2HgCl_2$.

Formyl derivative $C_{10}H_{17}.NHCHO$; [61°]; colourless glistening plates.

Acetyl derivative $C_{10}H_{17}.NHAc$: [141°] colourless plates.

Benzoyl derivative $C_{10}H_{17}.NHBz$: [131°]; colourless plates; insol. water and cold ligroïn (Leuchart a. Bach, *B.* 20, 104).

BORNYL BROMIDE $C_{10}H_{17}Br$. [75°]. From borneol and HBr (Kachler, *A.* 197, 98).

BORNYL CARBAMATE $C_{11}H_{19}NO_2$ *i.e.* $C_{10}H_{17}O.CONH_2$. [115°]. From sodium-borneol in toluene by the action of cyanogen (Haller, *C. R.* 93, 1511; 94, 869). Monoclinic needles (containing aq.). Sl. sol. hot water; sublimes partially at 100°. Dextrorotatory. Benzoic aldehyde and HCl form $CHPh(NH.CO.O.C_{10}H_{17})_2$ [187°]. *Cf.* CINEOL.

BORNYL CARBONATE $(C_{10}H_{17})_2CO_3$. [215°]. Extracted by boiling alcohol from the residue left in the preparation of cyano-borneol from sodium borneol and cyanogen (Haller, *C. R.* 94, 86). White plates or hexagonal tables, insol. water and alkalis, sl. sol. cold alcohol, sol. ether. May be sublimed. The rotatory power varies with that of the borneol from which it is prepared. Boiling alcoholic KOH gives K_2CO_3 and borneol.

BORNYL-CARBONIC ACID $C_{10}H_{17}O.CO_2H$. *Borneol-carboxylic acid.* From sodium-borneol and CO_2 (Baubigny, *Z.* 1868, 299; Kachler a. Spitzer, *M.* 2, 236; *C. C.* 1881, 359).—NaA': crystalline, v. sol. water; slowly decomposed by water with separation of borneol.

BORNYL CHLORIDE $C_{10}H_{17}Cl$. [157°].

Formation.—From borneol (1 pt.) and HCl (9 pts.) at 100° (Berthelot, *A.* 112, 366).

Preparation.—From PCl_5 (60g.), light petroleum, and borneol (45g. added in portions of 6g.). The product is shaken with water and the petroleum allowed to evaporate in the cold, when bornyl chloride separates (Wallach, *A.* 230, 231; Kachler, *A.* 197, 93; *B.* 11, 460).

Properties.—Crystals. V. sol. light petroleum, m. sol. alcohol. Lævorotatory.

Reactions.—1. Converted into HCl and camphene $C_{10}H_{16}$ [52°] (c. 160°), by heating with *water* (40 pts.) at 95° (Kachler, *A.* 197, 96); better by warming with aniline (W.). A little borneol is also formed by the action of water on bornyl chloride (Kachler, *A.* 200, 342; Riban, *A. Ch.* [5] 6, 382).—2. *Sodium* acting on a solution in benzene forms camphene $C_{10}H_{16}$ and hydrocamphene $C_{10}H_{18}$.

BORNYL-METHYL-UREA $C_{10}H_{17}.NH.CO.NHMe$. [200°]. Formed by the action of methyl cyanate upon bornylamine in ethereal solution. Plates. V. sol. ether and hot water (Leuchart a. Bach, *B.* 20, 108).

BORNYL OXIDE $C_{20}H_{34}O$ *i.e.* $(C_{10}H_{17})_2O$ (?). (285°–290°). Occurs in the essential oil of valerian (Bruylants, *B.* 11, 456). Not attacked by melted KOH.

BORNYL PHENYL-CARBAMATE $OC\left\langle\begin{matrix}NHC_6H_5\\ OC_{10}H_{17}\end{matrix}\right.$. *Bornyl-phenyl-urethane.* [133°]. Formed by the action of phenyl cyanate upon borneol. Needles. Sparingly sol. cold

ligroin and alcohol, v. sol. other solvents (Leuchart, *B.* 20, 115).

BORNYL-PHENYL-THIOUREA $C_{10}H_{17}.NH.CS.NHC_6H_5$. [170°]. Formed by the action of phenyl mustard-oil upon bornylamine in ethereal solution. Colourless needles. Nearly insol. ligroin (Leuchart a. Bach, *B.* 20, 109).

BORNYL-PHENYL-UREA $C_{10}H_{17}.NH.CO.NHC_6H_5$. [248°]. Formed by the action of phenyl cyanate upon bornylamine in ethereal solution. Silvery plates or fine needles. Sparingly soluble in ether and cold alcohol, easily in hot alcohol, insoluble in water (Leuchart a. Bach, *B.* 20, 108).

BORNYL-UREA $C_{10}H_{17}.NH.CO.NH_2$. [164°]. Formed by boiling bornylamine hydrochloride with potassium cyanate. Colourless needles. Easily soluble in hot water and alcohol (Leuchart a. Bach, *B.* 20, 108).

BORNESITE $C_7H_{14}O_6$. [175°]. $[\alpha]_D$ -32°. *Methyl-dambose.* A volatile substance occurring in the caoutchouc of Borneo. Sublimes at 205°. Sweet taste; does not ferment. After boiling with dilute acids it reduces Fehling's solution. At 120° it is split up by fuming HI into MeI and dambose (Girard, *C. R.* 73, 426).

BOROFLUORIDES, *v.* under BORON, FLUORIDE OF, p. 526.

BORON. B. At. w. 10·97. Mol. w. unknown, as V.D. has not been determined. S.G. amorphous not determined, but greater than 1·84 cryst. 2·53 2·68 (Wöhler, *A.* 141, 268; Hampe, *A.* 183, 75). S.H. about ·37 at 250°, probably about ·5 at 1000° (*v. post*; p. 525). Crystallises in dimetric forms, $a:c = 1:·5762$ (Sella, *P.* 100, 646); but crystals probably contained C and Al (*v. post*). S.V.S. about 4·1. Combines directly with O and Cl with production of much heat: $[B^2,O^3]$ = 317,200; $[B,Cl^3]$ = 104,000 (Troost a. Hautefeuille, *A. Ch.* [5] 9, 70). Chief lines in emission-spectrum are 2496·2, 2497, 3450·1 (Hartley, *T.* 175, 49).

Occurrence.—Not as boron; chiefly as borax and boric acid in volcanic districts, also as borate of Mg with $MgCl_2$ (*Boracite*), as borate of Ca with Ca silicate (*Datolite*), &c. Borax, or *tincal*, has been known in commerce for many centuries; boric acid was prepared from borax in 1702 by Homberg; the element was obtained by Gay-Lussac and Thénard in 1808 by deoxidising boric acid by potassium, which metal had been obtained by Davy the year before.

Formation.—1. By reduction of B_2O_3 by K (Gay-Lussac a. Thénard, *G. A.* 30, 363).—2. By reduction of $BF_3.KF$ by K (Berzelius, *P.* 2, 113).—3. By electrolysis of fused B_2O_3 (Davy, *G. A.* 35, 440).—4. By reduction of BCl_3 by H at a red heat (Dumas, *A. Ch.* 31, 376).—5. By fusing dry borax with amorphous P (Dragendorff, *C. C.* 1861, 865).—6. By heating $BF_3.KF$ or $BF_3.NaF$ with Mg (Wöhler a. Deville, *A. Ch.* [3] 52, 62; Geuther, *J. Z.* 2, 209).—7. By heating B_2O_3 with Mg and treating the product with HClAq (Jones, *C. J.* 35, 42).

Preparation.—AMORPHOUS. 10 parts fused B_2O_3 in coarse powder are mixed with 6 parts Na in small pieces, the mixture is placed in an iron crucible heated to full redness, 4 to 5 parts of fused NaCl are added, and the crucible is covered. When all action has ceased the molten mass is stirred with an iron rod, and the contents of the crucible, while still hot, are poured into water containing a little HCl. The NaCl, borax, and B_2O_3, dissolve, and the boron remains. The boron is washed with very dilute HClAq, then with alcohol, and then with ether; it is then dried at a very gentle heat (Wöhler a. Deville, *A.* 101, 113 a. 347; 105, 67).

CRYSTALLINE. Amorphous B is pressed as tightly as possible into a small Hessian crucible, a hole is then made in the mass and a rod of Al (4–6 grams) is placed in the hole: the crucible is covered and placed in another, larger, covered, crucible; the space between is filled with powdered charcoal, and the crucibles are heated to 1500° or 1600° for 1½ to 2 hours; after cooling the mass is treated with dilute HClAq which dissolves Al, and BN formed in the process (Wöhler a. Deville, *A.* 105, 67). According to Hampe (*A.* 183, 75) the crystals obtained by this process, or by any process said to yield crystalline B, contain Al, and some of them also C; Hampe gives the formula AlB_{12} to the black crystals, and $C_2Al_3B_{48}$ to the reddish-yellow crystals, obtained by the foregoing method (*v.* ALUMINIUM, BORIDES OF; and ALUMINIUM, BOROCARBIDE OF).

Properties.—Amorphous boron is a greenish-brown, opaque powder; tasteless; odourless; non-conductor of electricity; very infusible, but melts when placed between the poles of a battery of 600 Bunsen-cells. Said to be slightly soluble in water; Reinitzer (*Sitz. W.* 82, 736) supposes that the body which dissolves is a hydride of B (*v.* BORON, HYDRIDE OF). Insoluble in alcohol or ether. Heated *in vacuo* or in an inactive gas, *e.g.* H, B becomes darker in colour, heavier, and more compact. Heated in O, burns to B_2O_3, $[B^2,O^3]$ = 317,200: heated in air, B_2O_3 and BN are produced. Oxidised by heating with KNO_3, K_2CO_3, KOH, conc. HNO_3Aq, or *aqua regia*. Combines directly with many elements *e.g.* S, Cl, Br, N. The properties assigned by Wöhler a. Deville and others to crystalline B, are, according to Hampe's experiments, the properties of AlB_2, AlB_{12}, and $C_2Al_3B_{48}$ (*v.* ALUMINIUM, BORIDE OF, and BOROCARBIDE OF). The atom of B is trivalent in gaseous molecules (data BCl_3, BBr_3, BF_3). The atomic weight of B has been determined (i) by finding the V.D. of BCl_3 and BBr_3 and estimating the Cl and Br respectively in these compounds (Deville a. Dumas, *A. Ch.* [3] 55, 180); (ii) by dehydrating borax (Berzelius, *P.* 2, 129; 8, 19); (iii) by converting dehydrated borax into Na_2SO_4 by action of HFAq and H_2SO_4Aq (Berzelius, *P.* 2, 128; also Arfvedson, *P.* 2, 127); (iv) by determining the S. H. of boron (*v. infra*). Boron is a non-metallic element in its chemical reactions; its oxide, B_2O_3, is an anhydride; boric acid, $H_2B_2O_4$, corresponds in composition to nitrous acid, but thermal data show that boric acid is dibasic; the acids H_3BO_3 and $H_2B_4O_7$ (and several salts derived from the latter) are also known (*v.* BORON, OXYACIDS OF). B_2O_3 seems to form compounds with P_2O_5, SO_3, and WO_3. In some respects B shows analogies with C and Si:—physical properties; existence of acid containing F (HBF_4); direct combination with N; existence of many borotungstates; probable existence of a gaseous hydride, &c. In many points B resem-

ties N and P:—trivalency of B atom; composition of compounds (B_2O_3, $H_3B_2O_4$, BCl_3, $BOCl_3$, &c.); B_2S_3 not a salt-forming sulphide in reactions with sulphides of very positive metals; existence of a B analogue of tartar emetic, &c. Boron is the first member of Group III (periodic law); the succeeding members of this group are all decidedly metallic; but $Al_2O_3.3H_2O$ dissolves in KOHAq, and forms aluminates (*q. v.*); Al_2S_3 is also somewhat analogous to B_2S_3: the compositions of several B compounds are similar to those of the corresponding compounds of members of Group III., *e.g.* M_2O_3, MX_3 [X = Cl, Br]. $AlCl_3$ and BCl_3 combine directly with $POCl_3$. The differences between the chemical functions of B and the other elements of the group to which B belongs seem to be wider than is usual between the first and the following elements of the same group. The boron group comprises the following:

GROUP III.

Even Series	2.	4.	6.	8.	10.	12.
	B(11)	Sc(44)	Y(89)	La(139)	Yb(173)	–
Odd Series	3.	5.	7.	9.	11.	
	Al(27)	Ga(69)	In(114)	–	Tl(204).	

These elements are all metallic with the exception of B; in the reactions of B_2O_3 towards certain acids (p. 527) B shows that it may act as a feebly metal-like element. Boric acid is an extremely weak acid; its affinity is very small. The borates are very unstable salts, easily decomposed, even by water, to boric acid and basic oxides. The last member of the group, Tl, shows distinct analogies with the 11th series member of the next group, viz. Pb; B shows distinct analogies with the 2nd series member of the next group, viz. C. B occurs in Series 2, all the succeeding members of this series—C, N, O, F—are very negative and non-metallic; the general character of the series to which it belongs is stamped upon B, and the group-character is but feebly marked. It must, however, be remembered that very few compounds of B, except the borates and their derivatives, have been fully studied.

Specific heat. The S.H. of B as determined by Kopp, Regnault, and Mixter a. Dana (*A.* 126, 362; *Suppl.* 3, 1, 289; *J.* 1861. 29; *A.* 169, 388) varied from ·225 to ·262 for the temperature-interval 30°–70°. In 1873-4 Weber carefully determined the S.H. of crystallised boron (*v.* *P. M.* [4] 49, 161, 276); the following table summarises his results:

S.H. of crystallised boron.

t.	S.H.	S.H. × At w.
−40°	·1915	2·11
+77	·2737	3·01
177	·3378	3·72
233	·3663	4·03

The S.H. increases as temperature rises, but the rate of increase per 1° is much smaller at high than at low temperatures. The variations in the rate of increase are almost identical with those observed in the case of carbon (*q. v.*); assuming that this identity remains at temperatures above 233°, the value which the S.H. of crystallised boron will attain at about 1000° is approximately ·5. Weber did not analyse the crystals of boron used; they were prepared by heating boric acid with Al. According to Hampe's investigation crystals thus prepared are a definite compound of B and Al (*ante*, p. 524).

Reactions.—1. Heated in *air*, B_2O_3 and BN are formed.—2. Heated in *oxygen*, B burns to B_2O_3.—3. Heated to redness in N, BN is formed. 4. B combines directly with many elements, *e.g.* Cl, Br, S, and some metals (*v.* BORIDES).—5. *Water* is not decomposed by B at 100° but at a red heat. Steam reacts with B to form boric acid and H.—6. B is oxidised by heating with *nitric acid*, conc. *sulphuric acid*, or *aqua regia*; or by the action of molten *nitre*, or various *oxides of heavy metals*.—7. B is also oxidised by heating with *potash* (H is evolved), or with *alkaline carbonates* (C is separated, Berzelius, *P.* 8, 19), or with *phosphoric acid* (P is separated, Wöhler a. Deville, *A. Ch.* [3] 52, 63).—8. B burns when heated in *nitric oxide* forming B_2O_3 and BN; N_2O is without action on B.—9. At a red heat B decomposes *sulphuretted hydrogen*, *hydrogen chloride*, and *ammonia*, forming respectively B_2S_3 and H, BCl_3 and H, BN and H.—10. Many metallic chlorides and sulphides, *e.g.* $PbCl_2$, AgCl, PbS, are reduced to metal when heated with B.—11. From aqueous solutions of *gold chloride* B pps. Au.—12. Aqueous solutions of *caustic alkalis* do not react with B.—13. So called crystalline boron reacts similarly to amorphous boron, but the reactions occur only at high temperatures; it is oxidised with much difficulty.

References.—Gay-Lussac a. Thénard, *G. A.* 30, 363; Davy, *G. A.* 35, 440; Berzelius, *P.* 2, 113; Wöhler a. Deville, *A.* 101, 113; 103, 347; 105, 67.

Boron, Bromide of. BBr_3. Mol. w. 250·22. (90·5°) (Wöhler a. Deville, *A. Ch.* [3] 52, 89). S.G. 2·69 (W. a. D. *l.c.*). V. D. 127.

Formation.—1. By action of Br on B_2O_3 and C at red heat (Poggiale, *C. R.* 22, 127).—2. By heating B_2O_3 with PBr_5 (Gustavson, *B.* 2, 661).

Preparation.—Amorphous B is loosely packed into a glass tube, the tube is gently warmed and H is passed through it until every trace of moisture is removed; the H stream is stopped, the corks of the tube are removed for a moment or two, and then the B is gently heated in a stream of dry Br vapour, and the liquid BBr_3 is led into a dry flask surrounded by ice-cold water. The BBr_3 is freed from Br by digestion with Hg, and distillation.

Properties and Reactions.—Colourless, strongly fuming, liquid. Reacts with H_2O to form HBrAq and H_3BO_3Aq. Forms a compound with dry NH_3 (*v.* also Nicklès, *C. R.* 60, 800; Gautier, *C. R.* 63, 920).

Boron, Chloride of. BCl_3. Mol. w. 117·08. (18·23°) at 760 mm. (Regnault, *Acad.* 26, 658). S.G. 17° 1·35 (Wöhler a. Deville, *A. Ch.* [3] 52, 63). V. D. 58·2. H.F. [B, Cl³] = 104,000 (Troost a. Hautefeuille, *C. R.* 70, 185).

Formation.—1. By direct combination of B and Cl (Berzelius, *P.* 2, 147).—2. By the reaction of Cl with B_2O_3 and C at a red heat (Dumas, *A. Ch.* [2] 31, 436; 33, 376).—3. By the reaction of B with dry HCl.—4. By reaction between $HgCl_2$, $PbCl_2$, or AgCl, and amorphous B.—5. By heating B_2O_3 with PCl_5 to 150° for some days (Gustavson, *B.* 3, 426; 4, 975).

Preparation.—Amorphous B is heated in H until quite dry, then in dry Cl (details *v.* BORON, BROMIDE OF); the exit-end of the tube is connected with a Y tube, the upper part of which is surrounded with a mixture of snow and salt, and the lower limb passes into a dry tube also surrounded by snow and salt.

Properties. Colourless, highly refractive, liquid. Very expansible by heat. Fumes in air with decomposition.

Reactions.—1. With *water* forms H_3BO_3Aq and HClAq; $[BCl^3, Aq] = 79,200$ (Troost a. Hautefeuille, *A. Ch.* [5] 9, 70).—2. Not decomposed by heating with *zinc-dust* to 200°; or with *sodium* below 150°, at 150° B is separated.—3. Heated for some time with superficially oxidised sodium-amalgam at 150° B is separated (Gustavson, *B.* 3, 426).—4. Heated with P_2O_5, the compound $BCl_3.POCl_3$ is formed (*v. infra*) (Gustavson, *B.* 4, 975).—5. Heated with *sulphur trioxide*, B_2O_3 and SO_2Cl_2 are formed (Gustavson, *l.c.*).—6. With *alcohol* forms $B(OEt)_3$ and HCl.—7. With NO_2 reacts to produce $BCl_3.NOCl$, B_2O_3, and O (Geuther, *J. pr.* [2] 8, 854).

Combinations. 1. BCl_3 vapour passed into $POCl_3$ forms crystals of $BCl_3.POCl_3$ (Gustavson, *B.* 4, 975). This compound melts at 73° in a closed tube; by sublimation it separates into BCl_3 and $POCl_3$; it is decomposed by water, or moist air, into H_3PO_4Aq, H_3BO_3Aq, and HClAq. The same compound is produced by the reaction of BCl_3 with P_2O_5, and of B_2O_3 with $POCl_3$ (G. *l.c.*).—2. With *ammonia gas* gives $2BCl_3.3NH_3$, with production of much heat (Berzelius, *P.* 2, 147).—3. The compounds $BCl_3.CNCl$, and $BCl_3.CNH$, are known (Martius, *A.* 109, 80; Gautier, *C. R.* 63, 920).

Boron, Fluoride of. BF_3. Mol. w. 68·27. V. D. 33·7. S. (0°) 1043.

Formation.—1. By reaction, at white heat, of an intimate mixture of 1 part B_2O_3 with 2 parts CaF_2 free from silica; Gay-Lussac a. Thénard (*A. Ch.* 69, 204) prepared BF_3 by this method, in 1810, using vessels of flint, and collecting the gas over Hg.—2. By heating 1 part B_2O_3 with 2 parts CaF_2 and 12 parts conc. H_2SO_4Aq in glass vessels (J. Davy, *T.* 1812. 365); or 1 part B_2O_3, 1 part CaF_2, and 20 parts H_2SO_4 (Ferrari, *J. Ph.* 19, 48). Prepared thus, the gas always contains SiF_4 (Berzelius, *P.* 2, 116).

Preparation.—100 parts KBF_4 are mixed with 15–20 parts fused and finely powdered B_2O_3, and the mixture is heated with conc. H_2SO_4; the gas is collected over Hg (Schiff, *A. Suppl.* 5, 172).

Properties.—Colourless gas, with suffocating odour, condensed to a limpid liquid at −110° and strong pressure (Faraday, *A.* 56, 152). Acts on organic matter like conc. H_2SO_4; incombustible; not decomposed by electric sparks; does not act on glass; is very stable, not decomposed by Fe at red heat.

Reactions. 1. with *water* forms borofluorhydric acid HBF_4Aq (*v. infra*), or fluoboric acid $HBO_2.3HF$ (*v.* p. 530), according as the BF_3 is passed into water until the reaction is acid, or until the water is saturated (*v. infra*). $[BF^3, Aq] = 24,510$ (Hammerl, *C. R.* 90, 312).—2. *Conc. sulphuric acid* absorbs BF_3 (about 50 vols.), on adding water boric acid is ppd. (J. Davy, *T.* 1812. 365).—3. *Alkali*, and *alkaline earth, metals* react at red heat, forming borofluorides and B (Berzelius, *P.* 2, 138).—4. With *alcohol* boric acid and ether are formed.

Combinations. — With *ammonia* to form $BF_3.NH_3$, a solid body not decomposed by sublimation; also $BF_3.2NH_3$ and $BF_3.3NH_3$, liquids, decomposed by heat, by exposure to air, or by dry CO_2, giving NH_3 and $BF_3.NH_3$ (J. Davy, *T.* 1812. 368). According to Kuhlmann (*A.* 39, 320) BF_3 also combines with the oxides of N.

BOROFLUORHYDRIC ACID, AND BOROFLUORIDES. HBF_4, MBF_4. (*Hydrofluoboric acid.*) When BF_3 is led into water until the liquid shows a strongly acid reaction, and the liquid is cooled, ¼ of the B of the BF_3 separates as $H_2B_2O_4$ and the rest remains in solution in combination with H and F. By neutralising the liquid with KOHAq, and evaporating, a salt having the composition KBF_4 is obtained. If the acid liquid is evaporated HF is evolved, and $H_2B_2O_4.6HF$ remains in solution (*v.* FLUOBORIC ACID under BORON, OXYACIDS OF). According to Landolph (*C. R.* 86, 603) the acid HBF_4 may be obtained as a colourless liquid, boiling at 130° with partial decomposition, by the reaction between BF_3 and anethol ($C_6H_4.OCH_3.C_3H_5$): the acid reacts with a little water to produce HFAq and HBO_2Aq. A solution of HBF_4 is also obtained by dissolving crystallised boric acid in dilute, cooled, HFAq.

BOROFLUORIDES. These salts have been chiefly studied by Berzelius (*P.* 2, 113). They are obtained by the reactions between (1) metallic oxides or carbonates and HBF_4Aq, (2) BF_3 or $HBO_2.3HFAq$ and metallic fluorides, (3) HFAq and metallic fluorides mixed with HBO_2; in the last case half the metal of the fluoride usually forms an oxide. Most borofluorides are crystalline, soluble in water, decomposed by heat to BF_3 and metallic fluoride; heated with conc. H_2SO_4, BF_3, HBF_4Aq, and metallic sulphate, are produced; fused with alkali carbonates they form a mixture of alkali metal fluoride and alkali borate, this reaction affords the basis of a method for analysing the borofluorides (*v.* Marignac, *Fr.* 1, 105). Many borofluorides are partially decomposed by water forming so-called basic salts, *e.g.* $Ba(BF_4)_2.2H_2O$, $Ca(BF_4)_2$, $Pb(BF_4)_2$; some—*e.g.* the Ba or Pb salt—are partially decomposed by alcohol; the aqueous solutions of several—*e.g.* NH_4BF_4, $Ca(BF_4)_2$—redden blue litmus.

Potassium borofluoride KBF_4. Obtained as a gelatinous pp. by adding HBF_4Aq to a soluble K salt. Prepared by Stolba (*C. C.* 1872. 395) by heating to boiling 1 part crystallised boric acid, 2¼ parts powdered CaF_2, and 5¼ parts conc. H_2SO_4, cooling, filtering, pp.g. KBF_4 by addition of a soluble K salt, crystallising from hot water—S. (cold) 70.—The salt forms white lustrous six-sided tables; may be crystallised from alcohol or alkali carbonate solutions; melts when heated, and at a high temperature decomposes to BF_3 and KF.

The other borofluorides are $Al_2(BF_4)_6$, NH_4BF_4, $Ba(BF_4)_2.2H_2O$, $Ca(BF_4)_2$, $Cu(BF_4)_2$, $Pb(BF_4)_2$, $LiBF_4$, $Mg(BF_4)_2$, $NaBF_4$, $Y_2(BF_4)_6$, $Zn(BF_4)_2$.

Boron hydride. No hydride of B has been obtained free from H; but the experiments of Jones (*C. J.* 35, 41), and of Jones a. Taylor

(C. J. 39, 213), leave little doubt that a gaseous hydride exists and show that its composition is probably BH_3.

Preparation.—An intimate mixture of 1 part recently heated B_2O_3 and 2 parts Mg dust is placed in a Hessian or iron crucible, the lid is firmly wired down, and the crucible is heated in an ordinary fire; a violent reaction occurs, the crucible is at once removed from the fire; the fused mass—a mixture of B, Mg, Mg_3B_2, Mg_3N_2, and MgO—is placed in a small flask along with a little H_2O, and conc. HClAq is allowed to drop into the flask from a stoppered funnel tube; the gas is collected over water, or is dried by $CaCl_2$ and collected over Hg. Mg_3B_2 may also be prepared by direct combination of B and Mg, or by heating Mg in BCl_3 vapour (J. a. T., *C. J.* 39, 214). The gas consists of H mixed with a very small quantity of B hydride.

Analysis.—A known volume of pure H was burnt, by hot CuO, to H_2O, and the H_2O was weighed; an equal volume of the gas prepared as above was burnt in the same apparatus, and the H_2O was weighed; the excess of H_2O in the second experiment over that in the first gave a measure of the H combined with B as B hydride. The results showed the composition of the hydride to be BH_x where $x > 2$ and is approximately $= 3$.

Properties and Reactions.—Colourless, very disagreeable odour, sparingly soluble in water, solution seems to be unchanged on keeping. Gas burns with bright green flame producing H_2O and B_2O_3. Decomposed by passing through a hot tube to B and H. Reacts with $AgNO_3Aq$ producing small quantity of a black pp. containing B and Ag, and decomposed by H_2O giving B hydride. Reacts with $K_2Mn_2O_8Aq$ giving MnO_2 and H_3BO_3Aq. Combines with NH_3 (conc. NH_3Aq) to form a crystalline compound, of unknown composition, decomposed by acids.

References.—Older attempts to prepare hydride of boron: Wöhler a. Deville (*A. Ch.* [3] 52, 88); Genther (*J.* 1865. 125); Gustavson (*Z.* 1870. 521) (*v.* also Reinitzer, *Sitz. W.* 82, 736). Compounds of B with paraffin-radicles are known, *e.g.* BEt_3 (*v.* BORON, ORGANIC DERIVATIVES OF).

Boron, Hydroxides of, *v.* BORON, OXYACIDS OF.

Boron, Iodide of. Not known. Wöhler a. Deville (*A. Ch.* [3] 52, 90), by the action of I on B at a high temperature, obtained a body which they regarded as an oxyiodide. AgI does not react with B even at the melting point of Ag.

Boron, Nitride of. BN. Mol. w. unknown, as compound has not been gasified. Obtained in 1842 by Balmain by melting B_2O_3 with KCN (*P.M.* [3] 21, 170; 22, 467; 23, 71; 24, 191). Composition determined by Wöhler in 1850 (*A.* 74, 70).

Formation.—1. By heating B in N, or in NH_3.—2. By heating to whiteness a mixture of 4 parts B_2O_3 and 1 part charcoal powder in N. 3. By heating borax (Wöhler, *l.c.*), or boric acid (H. Rose, *P.* 80, 265), with NH_4Cl, or K_4FeCy_6 (W. *l.c.*), or KCN, or $Hg(CN)_2$, or urea (Darmstadt, *A.* 151, 255).—4. By heating $2BCl_3.3NH_3$ and passing the vapour, along with NH_3, through a hot tube (Martius, *A.* 109, 80). 5. By heating the compound of BCl_3 with NH_2Et to 200° (Gustavson, *Z.* [2] 6, 521).

Preparation.—A mixture of 1 part dehydrated borax and 2 parts NH_4Cl—or 7 parts B_2O_3 with 9 parts urea (Darmstadt, *l.c.*)—is strongly heated in a covered Pt crucible, the finely powdered mass is boiled with much water containing a little HCl, washed with hot water, B_2O_3 is removed by careful treatment with HFAq (Wöhler, *l.c.*, could not remove all B_2O_3 thus), and the BN is washed and dried.

Properties.—White, light, amorphous, powder; insoluble in water; infusible; soft (like talc) to the touch; heated in the edge of a flame exhibits greenish-white phosphorescence; very stable and very slightly acted on by most reagents, *e.g.* by heating in air, O, I, H, CO_2, or CS_2, or with conc. HClAq or HNO_3Aq or KOHAq.

Reactions.—1. At a very high temperature reacts with *chlorine*, to give BCl_3 (Darmstadt, *A.* 151, 255).—2. Heated to redness in *steam*, or to 200° in a closed tube with water, NH_3 and H_3BO_3 are formed.—3. With *molten potash*, NH_3 and K borate are produced. 4. With molten *potassium carbonate* KCNO and KBO_2 are formed, if much BN is used KCN is also produced.—5. *Oxides of Pb, Cu, or Hg* are reduced by heating with BN, with formation of NO or N_2O, (Wöhler, *A.* 74, 70).—6. Heated with conc. *sulphuric acid*, or with conc. *hydrochloric acid* to 200° in closed tubes, NH_3 and H_3BO_3 are formed.—7. With conc. *hydrofluoric acid* NH_4BF_4 is formed.—8. Heated in an *alcohol-flame fed with oxygen*, BN burns to B_2O_3.

Boron, Oxide of. B_2O_3. (*Boric anhydride.*) Mol. w. unknown, as compound has not been gasified. [577°] (Carnelley, *C. J.* 33, 278). S.G. 1·75–1·83 (Playfair a. Joule, *C. S. Mem.* 3, 57; *v.* also Ditte, *A. Ch.* [5] 13, 67). S.H. (16°–98°) ·2374 (Regnault, *A. Ch.* [3] 1, 129). H. F. [B^2,O^3] = 317,200 (Troost a. Hautefeuille, *A. Ch.* [5] 9, 70).

Preparation.—By heating B in O, or by strongly heating boric acid (*q. v.*).

Properties.—Semi-transparent, colourless, brittle, inodorous, glass-like, solid; volatilised at a very high temperature (Ebelmen, *A. Ch.* [3] 22, 211); volatilised in steam or alcohol-vapour; non-conductor of electricity (Lapschin a. Tichanowitsch, *P. M.* [4] 22, 308; Bowgoin, *C. R.* 67, 798).

Reactions.—B_2O_3 is a very stable compound; it is not decomposed by heating with powdered charcoal or with P vapour. It is an anhydride, but appears to show a feebly basic character in its reactions with certain acids (*infra* 6–8). 1. Heated with *potassium, sodium, or aluminium*, metallic oxide and B are formed.—2. Mixed with charcoal and heated in *nitrogen, chlorine, bromine*, or *carbon disulphide*, BN, BCl_3, BBr_3, or B_2S_3, is formed.—3. *Salts of most acids, e.g.* sulphates, nitrates, carbonates, are decomposed by heating with B_2O_3 to a high temperature, with production of borates and volatilisation of the acid (*v.* Tate, *C. J.* 12, 160).—4. Reacts with most *metallic oxides* at high temperatures to form borates.—5. With *water* forms boric acid (*q. v.*).—6. B_2O_3 is said to react with *fuming sulphuric acid* to form a compound $xB_2O_3.ySO_3.zH_2O$; the values given to x, y, and z by different chemists vary; thus Merz gives the for-

**mula $5B_2O_3.2SO_3.3H_2O$ (*J. pr.* 99, 181), and Schultz-Sellack gives the formula $B_2O_3.3SO_3.H_2O$ (*B.* 4, 15). This compound is easily decomposed by heat to B_2O_3 and SO_3.—7. B_2O_3 is said to form a compound with *phosphoric anhydride*, $B_2O_3.P_2O_5$; this body is produced by heating together H_3BO_3 and conc. H_3PO_4Aq (Vogel, *Z.* 1870. 125), and removing excess of the latter by hot water; it is also formed, according to Gustavson (*B.* 3, 426; 4, 975), by heating B_2O_3 with PCl_5 to 140° for 3-4 days, and also by heating B_2O_3 with $POCl_3$ to 150°-170° for 8 to 10 hours, distilling off the $POCl_3.BCl_3$ formed (*v.* BORON, CHLORIDE OF; *Combinations*, No. 1) and strongly heating the residual solid. $B_2O_3.P_2O_5$ is said to be insoluble in hot water, to be unacted on by acids, dissolved by boiling KOHAq, and to be decomposed by heating with Na, giving Na phosphide, and probably phosphide of B.—8. A compound of B_2O_3 with *tungstic anhydride* ($B_2O_3.9WO_3.xH_2O$) is described by Klein (*Bl.* [2] 36, 205), *v.* TUNGSTOBORATES, under TUNGSTEN.—9. B_2O_3 dissolves in *hydrofluoric acid*, forming $B_2O_3.6HF.H_2O$ (= $H_2B_2O_4.6HF$) (*v.* FLUOBORIC ACID, under BORON, OXYACIDS OF, p. 530).—10. When a solution of 1 part B_2O_3 and 2 parts $KH.C_4H_4O_6$ in 24 parts H_2O is evaporated to dryness at 100°, and the residue is treated with alcohol, a white, amorphous solid remains, insoluble in alcohol but very soluble in water. This solid has the composition $C_4H_4KBO_7$; its reactions are similar to those of tartar emetic; probably it is the K salt of an acid $B.C_4H_4O_6.OH$ analogous to the acid $Sb.C_4H_4O_6.OH$ obtained by Clarke a. Stallo (*B.* 13, 1787) (*v.* Meyrac, *J. Ph.* 3, 8; Soubeiran, *J. Ph.* 3, 399; 11, 560; 25, 741; 35, 241; Duflos, *S.* 44, 333; Vogel, *J. Ph.* 3, 1; Robiquet, *J. Ph.* [3] 21, 197; Wackenroder, *Ar. Ph.* [2] 58, 4; Wittstein, *R. P.* [3] 6, 1. 177; Duve, *J.* 1869. 540; Biot, *A. Ch.* [3] 11, 82; *v.* also under TARTRATES).

Boron, Oxyacids of, and their Salts. Three definite hydrates of B_2O_3 appear to be known; *orthoboric acid* $B_2O_3.3H_2O$ (= H_3BO_3), *metaboric acid* $B_2O_3.H_2O$ (= $H_2B_2O_4$), and *pyroboric* (or *tetraboric*) *acid* $2B_2O_3.H_2O$ (= $H_2B_4O_7$). Another hydrate $2B_2O_3.3H_2O$ was described by Berzelius (*S.* 23, 161) as obtained by heating H_3BO_3 'considerably over 100°.' Most metallic borates may be regarded as derived from $H_2B_2O_4$; some—*e.g.* borax—from $H_2B_4O_7$; a few are perhaps derived from $H_6B_4O_9$, *e.g.* $Ca_3B_4O_9$; and in addition to these several borates exist which at present must be regarded simply as compounds of B_2O_3 with metallic oxides (*v. infra*). All the boric acids are 'weak' acids, their salts are easily decomposed by reactions with other acids; the affinity of boric acid is extremely small, $Na_2B_2O_4$ in solution is entirely decomposed by an equivalent of H_2SO_4 (*Th.* 1, 209). Borates of the less positive metals are usually formed only by fusing together B_2O_3 and the metallic oxides. Many of these borates are decomposed by water; some of them are partially converted into carbonates when exposed to the action of moist air; borates even of the very positive metals readily combine with boric acid to form acid salts, but these salts, although containing excess of boric acid, usually turn red litmus blue; even alkali borates are partially decomposed by water. Thomsen's thermal investigation of boric acid proves that the acid obtained by dissolving B_2O_3 in water is dibasic; thus:—

m	$[m\mathrm{NaOHAq},B^2O^6Aq]$
1	11,101
2	20,010
3	20,460
6	20,640

The normal Na borate is therefore $Na_2B_2O_4$. When boric acid is added to a solution of this salt heat is produced; thus:—

m	$[Na^2B^2O^4Aq,mB^2O^3Aq]$
1	2,192
4	4,911

Acid salts are therefore probably formed, but the reaction of the solution towards litmus is still alkaline (*Th.* 1, 206).

ORTHOBORIC ACID. H_3BO_3 (*Boracic Acid*; *Boric Acid*). [184°-186°] (Carnelley, *C. J.* 33, 275).

Occurrence.—In the waters of many volcanic districts, *e.g.* in Tuscany; in many mineral springs; in combination with Na—as borax—in the waters of certain lakes in S. America, Thibet, Ceylon, &c.; in several minerals, *e.g. boracite* (borate of Mg), *boronatrocalcite* (borate of Ca and Na).

Formation. 1. By oxidising B with *aqua regia*, evaporating, dissolving in water, and recrystallising.—2. By dissolving B_2O_3 in water.

Preparation.—3 parts crystallised borax are dissolved in 12 parts boiling water, and (after filtering if necessary) 1 part conc. H_2SO_4 is added; boric acid separates on cooling. The crystals are gently heated, recrystallised from water, dried, fused in a Pt crucible (to remove all H_2SO_4), again recrystallised from water, and dried by pressure between filter paper.

Properties.—White, semi-transparent laminæ; triclinic (Miller, *P.* 23, 558), monoclinic (Kengott, *Sitz. W.* 12, 26). S.G. $\frac{15}{}$ 1·434 (Stolba, *J. pr.* 90, 457). S. (19°) 3·9, (25°) 6·72, (37·5°) 7·9, (50°) 9·84, (62·5°) 16·34, (75°) 21·15, (87·5°) 28·17, (100°) 33·67 (Brandes a. Firnhaber, *Ar. Ph.* 7, 50; *v.* also Ditte, *C. R.* 85, 1069). S.G. of H_3BO_3Aq saturated at 15° = 1·0248 (Stolba, *J. pr.* 90, 457). Heat of solution, $[H^3BO^3,Aq] = -5395$ (*Th.* 3, 196). Soluble in alcohol and several oils (Rose, *P.* 80, 262); soluble in warm conc. H_2SO_4, HCl, or HNO_3Aq, but most of the boric acid separates on cooling. Aqueous solution turns blue litmus wine-red, and turmeric paper cherry red; alcoholic solution burns with green-edged flame.

Reactions.—1. *Heated* to 100° $H_2B_2O_4$ is produced (Schaffgotsch, *P.* 107, 427; Bloxam, *C. J.* 12, 177; Merz, *J. pr.* 99, 179); heated to 140° for a long time, or to 160° in a current of dry air, $H_2B_4O_7$ is formed (Merz, *l.c.*; Ebelmen a. Bouquet, *A. Ch.* [3] 17, 63); heated to about 300° the oxide B_2O_3 remains. Berzelius (*S.* 23, 161) said that $H_6B_4O_9$ (= $2B_2O_3.3H_2O$) is formed by heating H_3BO_3 to a temperature 'considerably above 100°'; Merz (*l.c.*) affirmed the production of $8B_2O_3.H_2O$ at 270°.—2. Boiling conc. H_3BO_3Aq dissolves a few *metallic sulphides and oxides* (Tissier, *C. R.* 39, 192; 45, 411); decomposes *alkali* and *alkaline earth carbonates* (Popp, *A. Suppl.* 8, 10).—3. With *alkalis* and *alkali-carbonates* salts of the form

$M_2B_4O_7$ or $M_2B_4O_7.xH_2B_4O_7$ are generally produced; few metallic salts of the form M_3BO_3 are certainly known; hence H_3BO_3Aq reacts as $H_2B_4O_7Aq$ (v. also BORATES). Ethereal salts of H_3BO_3—e.g. Et_3BO_3, Me_3BO_3—are known, but none of them is directly formed from H_3BO_3 (p. 530).

METABORIC ACID, $H_2B_2O_4$; and PYROBORIC or TETRABORIC ACID, $H_2B_4O_7$. Formed by heating H_3BO_3 (v. *supra*); glass-like, amorphous solids. Some salts of $H_2B_2O_4$ are obtained by the reaction between $H_2B_2O_4Aq$ and alkalis; salts of $H_2B_4O_7$ are obtained indirectly (v. *infra*).

BORATES. No borate is quite insoluble in water; the alkali borates are very soluble. The less soluble borates are easily decomposed by water, the easily soluble salts are also decomposed, but less quickly; an alkali borate, for instance, in conc. aqueous solution slightly reddens litmus, but when much water is added the litmus becomes blue. Solutions of alkali borates absorb CO_2 and H_2S; they decompose NH_4 salts when boiled with them; dilute solutions react with Hg and Ag salts similarly to alkali solutions. A few borates can be obtained as definite, fairly stable, salts by precipitation from solutions; $KHB_2O_4.2H_2O$ separates from a solution of K_2CO_3 in excess of B_2O_3Aq to which much KOHAq has been added; $MgB_2O_4.4H_2O$ is said to be formed by the reaction between borax solution and $Mg2NO_3Aq$. The more definite borates are generally obtained by melting together B_2O_3 and basic oxides. As a class the borates very readily undergo change; the composition of very many is therefore extremely doubtful. H. Rose, who investigated many borates, did not attempt to wash his preparations, but pressed them between filter paper till dry, and then determined the quantities of the admixed foreign salts. Most borates seem to belong to the two forms $M_2B_2O_4$ and $M_2B_4O_7$; many may be represented as $M_2B_2O_4.xH_2B_2O_4$ and $M_2B_4O_7.xH_2B_4O_7$; a few—e.g. $3M_2O.B_2O_3$—may be regarded as derivatives of H_3BO_3. The best-marked borates are the salts of K and Na.

Potassium borates.—(1) *Normal metaborate*, $K_2B_2O_4$. Monoclinic crystals ($a:b:c$ = 2·744:1:2·676); by melting, at white heat, 1 part B_2O_3 with 1·95 parts K_2CO_3, dissolving in water, evaporating to a syrup out of contact with air, and crystallising (Schabus, *Bestimmung der Krystallgestalten &c.* (Wien, 1855), 31). (2) *Acid metaborate*, $K_2B_2O_4.H_2B_2O_4.4H_2O$. Regular six-sided prisms; by saturating boiling K_2CO_3Aq with B_2O_3Aq, adding KOHAq to strongly alkaline reaction, evaporating, and crystallising (Laurent, *A. Ch.* [2] 67, 215). Said to sometimes crystallise with $5H_2O$ in rhombic prisms; and to lose H_2O when heated in a closed vessel.—(3) *Other acid salts*. $K_2B_2O_4.2H_2B_2O_4.6H_2O$, obtained like (2), but using less KOHAq. $2K_2B_2O_4.4H_2B_2O_4.5H_2O$ (or $4H_2O$), by adding B_2O_3Aq to boiling K_2CO_3Aq until solution has a slightly acid reaction (Rammelsberg, *P.* 95, 199; Reissig, *A.* 127, 33).

Sodium borates.—(1) *Normal metaborate*, $Na_2B_2O_4.4H_2O$. Large monoclinic prisms; by fusing 1 part dry Na_2CO_3 with 1·17 parts B_2O_3 (or with 3·6 parts crystallised borax), dissolving in water, and crystallising out of contact with air. Melts at 57°; salt with $3H_2O$ separates on cooling. Mixed with NaF, in solution, and crystallised, the salt $Na_2B_2O_4.6NaF.H_2O$ separates (v. FLUOBORIC ACID) (Hahn, *J.* 1859. 128).—(2) *Acid metaborates*. $Na_2B_2O_4.3H_2B_2O_4.7H_2O$, lustrous, hard, crystalline crust, obtained by boiling solution of 2 equivs. borax with 1 equiv. NH_4Cl so long as NH_3 is evolved, and crystallising (Bolley, *A.* 68, 122). $Na_2B_2O_4.4H_2B_2O_4.7H_2O$, small crystals obtained by dissolving in water 1 equiv. borax with 5 equivs. H_3BO_3, and crystallising (Laurent, *C. R.* 29, 5).—(3) *Orthoborate*, Na_3BO_3. Said to be formed by fusing B_2O_3 with excess of NaOH (Bloxam, *C. J.* 14, 143). (4) *Tetra*, or *pyro*, *borates*. (a) Borax. $Na_2B_4O_7.10H_2O$, ordinary or prismatic borax; $Na_2B_4O_7.5H_2O$, octahedral borax. The former occurs native; it is obtained by purifying crude borax, or by fusing 1 part dry Na_2CO_3 with 2·34 parts H_3BO_3, dissolving in warm water, and slowly crystallising from a solution of S.G. 1·14–1·15 (B.P. 104°), stopping when the temperature has fallen to 25°–30°. The salt with $5H_2O$ separates from aqueous solutions of ordinary borax of S.G. 1·246 at temperatures between 56° and 79°, or from supersaturated solutions of the same salt protected from dust, or from aqueous solutions of any strength evaporated at 10° to 12° (Gernez, *C. R.* 78, 68). *Ordinary borax* crystallises in large, transparent, colourless, doubly refractive, monoclinic prisms ($a:b:c$ = 1·0995:1:·5629. β = 73°25′). S.G. 1·69 (Filhol, *A. Ch.* [3] 21, 415). S. (0°) 2·8, (20°) 7·9, (40°) 17·9, (60°) 40·4, (80°) 76·2, (90°) 119·7, (100°) 201·4 (Poggiale, *A. Ch.* [3] 8, 463). S.G. of solution saturated at 15° = 1·0199 (contains 38·491 borax) (Michel a. Krafft, *A. Ch.* [3] 41, 471). Insol. in alcohol. Heat disappears during solution; $[Na^2B^4O^7.10H^2O,Aq]$ = –25,860 (Thomsen). S.H. (19°–50°) ·385 (Kopp, *T.* 155, 71). Refractive indices (23°, Na light) for α = 1·4463, for β = 1·4682, for γ = 1·4712 (Kohlrausch, *W.* 4, 1). The crystals effloresce in air (according to Sims only when they contain sodium carbonate); when heated they melt and give off $10H_2O$, leaving *burnt borax* ($Na_2B_4O_7$), which melts at a red heat to a glass-like mass (*vitrified borax*) of S.G. 2·36; exposed to moist air this takes up $10H_2O$. Solution of borax in water is alkaline to litmus; it dissolves many organic compounds more readily than water, e.g. benzoic acid and gallic acid; some compounds insoluble in water dissolve in borax solution, e.g. stearic acid, various gums, resins, and oils; As_2O_3 dissolves easily; silicic acid only very slightly. Molten borax dissolves many metallic oxides and salts forming fusible double salts; hence its use as a flux, and also in analysis. Crystals of *corundum* were obtained by Ebelmen (*A.* 80, 205) by dissolving Al_2O_3 in molten borax, and crystals of *rutile* and *tridymite* by dissolving TiO_2 and SiO_2, respectively, in the same solvent (v. Rose, *J. pr.* 101, 228; 108, 208). *Octahedral borax* crystallises in hard, transparent, regular octahedra. S.G. 1·8. Unchanged in dry air, but in moist air changed to prismatic borax. Melts to a glass-like mass.

(b) Amorphous tetraborate. $Na_2B_4O_7.4H_2O$. Obtained according to Schweizer (*A.* 76, 267) by evaporating aqueous borax

solution at 100° and drying the residue at the same temperature for a long time.

(c) $Na_2B_4O_7.6H_2O$ was found by Bechi (*Am. S.* [2] 17, 129; 19, 120) in an old lagoon; it has not been prepared artificially.

The remaining borates have been chiefly investigated by Berzelius (*S.* 23, 160; *P.* 2, 113; 9, 433; 33, 98; 34, 561); Arfvedson (*Gm.-K.* 6th ed.); Gmelin (*v. Gm.*); H. Rose (*P.* 9, 176; 19, 153; 86, 561; 87, 1, 470, 587; 88, 299, 482; 89, 473; 91, 452); Wöhler (*P.* 28, 525); Rammelsberg (*P.* 49, 445); Ebelmen (*A. Ch.* [3] 16, 129; 17, 54; 33, 31); Bouquet (*A. Ch.* [3] 17, 54); Bolley (*A.* 68, 122); Herapath (*P. M.* [3] 34, 375); Laurent (*A. Ch.* [2] 67, 215); Tissier (*C. R.* 39, 192; 45, 411); Bloxam (*C. J.* 12, 177; 14, 143). For an account of various supposed compounds of MO with B_2O_3 *v.* Ditte (*A. Ch.* [5] 30, 218). The following are the salts which have been chiefly examined; but the composition of many is not settled.

Aluminium. $2Al_2O_3.B_2O_3.3H_2O$; $3Al_2O_3.2B_2O_3.7H_2O$ (H. Rose). — $3Al_2O_3.B_2O_3$ (Ebelmen).

Ammonium.— $(NH_4)_2B_2O_4.H_2B_2O_4.2H_2O$ (also $3H_2O$) (Arfvedson). — $(NH_4)_2B_2O_4.5H_2B_2O_4.4H_2O$ (Bechi, *Am. S.* [2] 17, 129; 19, 120).

$(NH_4)_2B_2O_4.3H_2B_2O_4.3H_2O$ (Gmelin).—

$(NH_4)_2B_2O_4.4H_2B_2O_4.2H_2O$ (Rammelsberg).

Barium.—$BaB_2O_4.10H_2O$ (Berzelius).— $BaB_2O_4.H_2O$ (Rose). — $BaB_2O_4.H_2B_2O_4.4H_2O$; $BaB_2O_4.2H_2B_2O_4.12H_2O$; $2BaB_2O_4.H_2B_2O_4.11H_2O$ (Laurent).— $Ba_3(BO_3)_2$; $2BaO.B_2O_3$; $5BaO.2B_2O_3$ (Bloxam). $2BaO.3B_2O_3$; BaB_4O_7 (Ditte, *C. R.* 77, 788).

Cadmium. CdB_2O_4; $2CdB_2O_4.CdO_2H_2.2H_2O$ (Rose).

Calcium.—

$CaB_2O_4.2H_2O$; $2CaB_2O_4.H_2B_2O_4.4H_2O$ (Rose).—

$CaB_2O_4.H_2B_2O_4$ (Tünnermann).—

$CaB_2O_4.3H_2B_2O_4.6H_2O$ (Laurent).—

CaB_2O_4; $3CaO.2B_2O_3$; $2CaO.3B_2O_3$;

$3CaO.3MgO.4B_2O_3$ (Ditte).

Cobalt. $2CoB_2O_4.CoO_2H_2.3H_2O$ (Rose).

Copper. Composition very uncertain (*v.* Tünnermann, Rose, Laurent, Bolley; also le Roux, *C. R.* 64, 126; Pasternack, *A.* 151, 227; Poussier, *B.* 6, 1138).

Didymium. $DiBO_3$ (Clève, *Bl.* [2] 43, 364).

Iron.— $Fe(B_2O_4)_3.3H_2O$; found in a lagoon-crater (Bechi, *Am. S.* [2] 17, 129; 19, 120). Basic salts of uncertain composition are formed by the reactions between alkali borates and solutions of ferric salts; borates of Fe and Na seem to be produced by ppg. iron alum with alkali borates (Rose).

Lead. $PbB_2O_4.H_2O$; $2PbB_2O_4.H_2B_2O_4.3H_2O$; $PbB_2O_4.H_2B_2O_4.3H_2O$ (Herapath; *v.* also Rose). Double salts: $PbB_2O_4.Pb(NO_3)_2.H_2O$;

$PbB_2O_4.PbCl_2.H_2O$ (Herapath).

Magnesium.— $MgB_2O_4.4H_2O$; $MgB_2O_4.2H_2B_2O_4.6H_2O$; $MgB_2O_4.3H_2B_2O_4.8H_2O$; $MgB_2O_4.5H_2B_2O_4.13H_2O$ (Laurent; Rammelsberg). — $MgB_2O_4.8H_2O$ (Wöhler). — $Mg_3(BO_3)_2$ (Ebelmen). Double salts: $6MgO.3X_2O_3.2B_2O_3$ (X = Cr or Fe) (Ebelmen). Ditte describes various compounds of the form $xMgO.yCaO.zB_2O_3$.

Nickel.— $NiB_2O_4.2H_2O$ (Rose): also various vague basic salts.

Rubidium.— $Rb_2B_4O_7.6H_2O$ (Reissig, *A.* 127, 33).

Silver.—$Ag_2B_2O_4.H_2O$; $3Ag_2O.4B_2O_3$ (Rose).

Strontium.—SrB_2O_4; SrB_4O_7; $3SrO.2B_2O_3$; $2SrO.3B_2O_3$ (Ditte). — $3SrB_2O_4.2H_2B_2O_4.5H_2O$ (Rose).— $SrB_2O_4.H_2B_2O_4.3H_2O$;

$SrB_2O_4.3H_2B_2O_4.3H_2O$ (Laurent).

Zinc.—Very vague (*v.* Rose). Büscher (*A.* 151, 234) describes the double salt

$ZnO.4NH_3.2B_2O_3.6H_2O$.

[? *Samarium borate.*— $SmBO_3$ (Clève, *Bl.* [2] 43, 170.]

FLUOBORIC ACID, and FLUOBORATES. B_2O_3 appears to react as a feebly basic oxide towards the anhydrides of a few acids, *e.g.* SO_3 and P_2O_5 (*v.* BORON, OXIDE OF, *Reactions*, Nos. 6, 7). H_3BO_3 dissolves in conc. HFAq; by concentration, and cooling over H_2SO_4, a thick syrup-like liquid is obtained (S.G. 1·584) containing $H_2B_2O_4$ and HF in the ratio $H_2B_2O_4$:6HF. This liquid is generally regarded as a definite acid, called *fluoboric acid.* This liquid chars organic matter like H_2SO_4. The same liquid is obtained by saturating water with BF_3 and distilling (Gay-Lussac a. Thénard, *Recherches physico-chimiques*, 2, 38; Berzelius, *P.* 58, 503; 59, 644). The liquid is decomposed by water into HBF_4Aq and $H_2B_2O_4$ (*v.* BOROFLUORHYDRIC ACID, under BORON, FLUORIDE OF). If this liquid is neutralised by NaOHAq or KOHAq, and the solution is evaporated, the salts $M_2B_2O_4.6MF.H_2O$ (M = Na or K) are obtained (Berzelius). The same salts are also formed, when M = K by fusing KF with H_3BO_3, and when M = Na by crystallising mixed solutions of $Na_2B_2O_4$ and NaF. It is very doubtful whether the so-called fluoboric acid is a definite compound or not. According to Basarow (*C. R.* 78, 1698) the liquid prepared as described is decomposed by distillation; at 140° BF_3 is given off, at 160° to 170° a thick, heavy, fuming liquid (S. G. 1·77) comes over, at 175°–185° a less fuming liquid is produced, and as the temperature rises the distillate becomes lighter and fumes less in air. The heavy distillates are decomposed by water with separation of H_3BO_3. The salts obtained by Berzelius are separated by crystallisation into MF, which crystallises out first, and a mixture of MF with $M_2B_2O_4$ (Basarow). Solution of the so-called acid reacts with $AgNO_3Aq$ to give $Ag_2B_2O_4$ and Ag_2O. Basarow regards fluoboric acid as a mixture of $H_2B_2O_4$ with HBF_4 and HF. Landolph (*B.* 12, 1583) describes the bodies $H_4B_2O_5.3HF$ and $H_4B_2O_5.2HF$; the first is obtained in small quantities by the reaction between BF_3 and C_5H_{10}, the second is one of the products of the action of BF_3 on hot anethol. Both bodies are fuming, acid, liquids; they seem to be fairly stable; the first is unchanged by distillation.

BOROTUNGSTATES. Many compounds of the form $xB_2O_3.yWO_3.zMO$ (MO = metallic oxide) have been obtained; the acid $B_2O_3.9WO_3.2H_2O.18aq$ has been prepared. The principal borotungstates will be described under TUNGSTEN as TUNGSTOBORATES.

Detection and Estimation of Boric Acid. Free boric acid is detected by its action on turmeric paper, or by the green colour which it imparts to the flame of burning alcohol; borates do not give these reactions, therefore they must be decomposed by H_2SO_4Aq before applying the alcohol test, or by HClAq before applying the

curcuma paper test. There is no very satisfactory method for estimating boric acid. The most insoluble salt is KBF_4; it is obtained from boric acid or borates by adding excess of KOHAq, then evaporating with excess of HFAq, dissolving out sulphate, nitrate, &c. of K, by $KC_2H_3O_2$Aq, washing with alcohol, and drying at 100°. Marignac (*Fr.* 1, 405) evaporates the solution of the borate with excess of NH_4ClAq and $MgCl_2$Aq, with various precautions, and finally obtains a mixture of MgO and Mg borate in which he then estimates the amount of MgO and so gets the amount of boric acid (*v.* also Ditto, *C. R.* 80. 490 a. 561). As boric acid interferes with estimation of some other bodies, *e.g.* phosphoric acid, it is sometimes necessary to remove it; this may be done either by boiling with alcohol and H_2SO_4Aq (Et_3BO_3 goes off), or with HF and H_2SO_4Aq (BF_3 goes off). Rosenbladt (*Fr.* 26, 18) describes a method based on the volatilisation of boric acid by distillation with methylic alcohol; the method gives good results (*v.* also Gooch, *C. N.* 55, 7).

Boron, oxychlorides of. Two are known, BOCl and $BOCl_3$; neither exists as a gas; both are decomposed by heat. BOCl is a white gelatinous solid, obtained by heating B_2O_3 with BCl_3, in the ratio B_2O_3:2BCl_3, to 150°; at a high temperature it is decomposed to BCl_3 and B_2O_3 (Gustavson, *Z.* 1870. 521). $BOCl_3$ is described as a yellowish-green liquid; it was obtained, along with BCl_3, by passing Cl over a heated mixture of B_2O_3 and C, removing Cl from the gaseous products by Cu turnings, condensing, and removing BCl_3 by evaporation (Councler, *J. pr.* [2] 18, 399). The conditions under which $BOCl_3$ is formed are not definitely known; Councler obtained the best results when relatively little carbon was used, and a fairly rapid stream of Cl was passed through the tube. $BOCl_3$ is decomposed by heat into BCl_3, B_2O_3, and Cl; and by water to H_3BO_3, HCl, and Cl. No oxychloride of B is formed by the action of ozone on BCl_3, or by passing electric sparks through a mixture of BCl_3 and O (Michaelis a. Becker, *B.* 14, 914).

Boron, sulphide of. B_2S_3. Mol. w. unknown, as compound has not been gasified.

Formation.—1. By heating B in S vapour to white heat (Berzelius, *P.* 2, 145).—2. By gently heating B in dry H_2S (Wöhler a. Deville, *A.* 105, 72).

Preparation. Small pellets are made by mixing powdered B_2O_3 with soot and oil and heating out of contact with air; these are heated to full redness in a porcelain tube, in a stream of dry CS_2; the tube is connected with two small flasks surrounded by snow and salt. The B_2S_3 collects on the surface of the condensed CS_2; it is separated from CS_2 and dried in an atmosphere of H (Fremy, *A. Ch.* [3] 38, 312). B_2S_3 is a white solid (with a yellowish tinge, Fremy), consisting of groups of small crystals; it smells strongly, and its vapour acts on the eyes; it is rapidly decomposed by moisture to B_2O_3 and H_2S; it may be melted in an atmosphere of H, and volatilised in a current of H_2S.

M. M. P. M.

BORON, ORGANIC DERIVATIVES OF.

Boron tri-methide C_3H_9B *i.e.* BMe_3. V.D. 1·91 (calc. 1·93). From ethyl borate and $ZnMe_2$, thus: $2B(OEt)_3 + 3ZnMe_2 = 2BMe_3 + 3Zn(OEt)_2$ (Frankland, *C. J.* 15, 373). Pungent gas. V. sl. sol. water, v. sol. alcohol and ether. Takes fire in air, burning with a green flame. Not affected by conc. H_2SO_4 or by HI. Combines with potash forming BMe_3KOH. Combines with ammonia forming BMe_3NH_3 [56°] (110°). Combines also with NaOH, CaO, and BaO.

Boron tri-ethide BEt_3. Mol. w. 98. (95°). S.G. 23: ·696. V.D. 3·40 (calc. 3·40). From BCl_3 or $B(OEt)_3$ and $ZnEt_2$ (Frankland, *Tr.* 1862, 167; *Pr.* 25, 165). Pungent oil. Takes fire in air. Slowly decomposed by HCl, evolving C_2H_6. Violently attacked by chlorine.

Combinations.—1. With *ammonia* it forms a liquid BEt_3NH_3. 2. By careful oxidation, first in air, then in oxygen, it forms an *oxide* BEt_3O_2 (125°). Water decomposes this oxide, forming ethyl-boric acid, $BEt(OH)_2$. Ethyl-boric acid is crystalline, and may be sublimed; its solutions are acid, but it does not form salts. A compound $BEt(OEt)_2B(OEt)_3$ (*c.* 112°) appears to be formed by the action of $ZnEt_2$ (1 mol.) on boric ether; it is decomposed by water into alcohol, $BEt(OH)_2$ and $B(OH)_3$; and by $ZnEt_2$ it is converted into $BEt_2(OEt)$ (103°), which absorbs oxygen, becoming $BEt(OEt)_2$. Di-ethyl-boric ether, $BEt_2(OEt)$ is saponified by water, and the acid absorbs oxygen, becoming crystalline BEt(OEt)(OH), which is converted by water into ethyl-boric acid $BEt(OH)_2$.

Boron-phenyl-di-chloride $C_6H_5BCl_2$. [about 0°]. (175°). Prepared by heating boron trichloride with mercury di-phenyl at 200° (Michaelis a. Becker, *B.* 15, 180). Colourless fuming fluid. By the action of water it gives phenyl-boric acid, and by the action of alcohol, phenyl-boric ether.

Boron-*p*-tolyl-dichloride $C_6H_4(CH_3).BCl_2$. [27°]. Colourless crystals. Prepared by heating boron tri chloride with mercury di-*p*-tolyl (Michaelis a. Becker, *B.* 15, 185).

BORO-TARTAR EMETIC *v.* BORON, OXIDE OF; *Reactions*, No. 10; also under TARTRATES.

BOROTUNGSTATES. Compounds of the form $xB_2O_3.yWO_3.zMO$ (M = metal), *v.* TUNGSTOBORATES, under TUNGSTEN.

BRASILEIN *v.* BRAZILEÏN.

BRASS *v.* COPPER, ALLOYS OF.

BRASSIC ACID $C_{22}H_{42}O_2$. [60°]. Prepared by just melting its isomeride, erucic acid, with dilute HNO_3, and adding sodium nitrite. Laminæ (from alcohol). Combines with bromine. Potash-fusion gives arachic acid.

Salts. NaA': laminæ (from alcohol).

Ethyl ether EtA': [30°]; (above 360°); glistening plates; obtained by etherifying the acid or by the action of nitrous acid upon ethyl erucate.

Glycerin-di-brassic ether $C_3H_5(OH)A'_2$: (*dibrassidin*) [65°]; crystals, sl. sol. ether. Formed from glycerin-di-erucic ether by nitrous acid.

Glycerin-tri-brassic ether $C_3H_5A'_3$: *Tribrassidin.* [47°], after heating [36°]; colourless crystalline powder; v. sol. ether, nearly insol. alcohol. Obtained by the action of nitrous acid upon rape-seed oil, and crystallisation of the solid product from ether.

Amide $C_{21}H_{41}.CONH_2$: [90°]; colourless

needles; formed by the action of NH_3 gas upon the anhydride.

Anilide $C_{21}H_{41}.CONHPh$: [78°].

Anhydride $(C_{21}H_{41}.CO)_2O$: [29°]; glistening tables; v. sol. ether and benzene, insol. alcohol and water; formed by the action of PCl_3 upon brassic acid and subsequent addition of alcohol (Reimer a. Will, *B.* 19, 3320; *cf.* Wesky, *J. pr.* 58, 449; Haussknecht, *A.* 143, 40; Fitz, *B.* 4, 444; Goldschmiedt, *Sitz. B.* 74, 394).

BRASSYLIC ACID $C_{11}H_{20}O_4$. Mol. w. 216. [109°]. Formed, together with its aldehyde and dioxybehenolic acid, by the action of fuming HNO_3 on behenolic acid (Haussknecht, *A.* 143, 45). Crystalline, v. sl. sol. cold water, v. sol. alcohol and ether.

Salts.—CaA″ 3aq.—Ag_2A''.

BRASSYLIC ALDEHYDE $C_{11}H_{20}O_3$. The chief product of the action of fuming HNO_3 on behenolic acid (*v. supra*). Oil, lighter than water, volatile with steam. Sol. NaOHAq and reppd. by HCl. Oxidised by bromine to brassylic acid.

BRAZILEÏN $C_{16}H_{12}O_5H_2O$.

Formation.—By the oxidation of brazilin by air in presence of alkalis, or in ethereal solution by HNO_3 (Reim, *B.* 4, 334; E. Kopp, *B.* 6, 446; Liebermann a. Burg, *B.* 9, 1883; Buchka a. Erck, *B.* 18, 1142).

Preparation.—Extract of Brazil-wood is dissolved in hot water and, after cooling, NH_3 in slight excess is added. The solution is exposed to air, when a pp. is formed which is crystallised from hot dilute acetic acid (Hummel a. A. G. Perkin, *C. J.* 41, 373).

Properties.—Minute crystals with grey lustre. Reddish-brown when powdered. Very slightly soluble in cold water, more so in hot water. The solution is yellowish-pink with greenish-orange fluorescence. Alkaline solutions are carmine red, but slowly turn brown in air.

Reactions.—1. If hot glacial acetic acid be slowly added to a solution in cold conc. H_2SO_4, minute orange needles of *iso-brazileïn sulphate*, $C_{16}H_{11}O_4SO_4H$, are got. Its alkaline solutions are carmine red quickly turning brown in air. Alcohol turns iso-brazileïn sulphate scarlet, forming the basic salt $C_{16}H_{12}O_5 2(C_{16}H_{11}O_4SO_4H)$. 2. Conc. HCl at 100° forms $C_{16}H_{11}O_4Cl$. Minute red prisms with violet lustre, called iso-brazileïn chlorhydrin. Its aqueous solution is orange.—3. HBr at 100° forms, similarly, $C_{16}H_{11}O_4Br$. Brazileïn resembles hæmateïn (*q. v.*) in these reactions.

BRAZILIN $C_{16}H_{14}O_5$. Occurs in Brazil-wood (the wood of *Cæsalpinia crispa*) and in Sapanwood (from *Cæsalpinia Sapan*) (Chevreul, *A. Ch.* 66, 226; E. Kopp, *B.* 6, 447; Bolley, *J. pr.* 93, 451).

Preparation.—The dark brownish-red crusts deposited during the preparation and storage of commercial extract of Brazil-wood consist of brazilin and its lime compound. The crusts are washed with dilute (5 p.c.) HCl and then extracted with very dilute (12 p.c.) alcohol.

Properties.—Colourless crystals (containing aq). Sol. water, alcohol, and ether. Turns orange in air. Forms a carmine solution in aqueous NaOH in air; this solution is bleached by zinc-dust, but re-oxidised to brazileïn by air. Aqueous solutions are also turned red by NH_3 or baryta when exposed to air.

Reactions.—1. Resorcin is among the products of its *dry distillation.*—2. $KClO_3$ and HCl give iso-tri-chloro-glyceric acid (Benedikt, *A.* 178, 100).

Salt.—PbA″aq: small colourless needles.

Tri-acetyl-derivative $C_{16}H_{11}(OAc)_3O_2$: [106°]; slender colourless needles.

Tetra-acetyl-derivative $C_{16}H_{10}(OAc)_4O$: [151°]; glistening needles (Buchka a. Erck, *B.* 18, 1138).

BREIDIN *v.* ARBOL-A-BREA.

BRIMSTONE *v.* SULPHUR.

BRITANNIA METAL *v.* TIN, ALLOYS OF.

BRITISH GUM *v.* DEXTRIN.

BROMAL *v.* BROMO-ACETIC ALDEHYDE.

BROMALIDE $C_5H_2Br_6O_3$ *i.e.*

$CBr_3.CH\left\langle{CO.O \atop O}\right\rangle CH.CBr_3$. *Tri-bromo-ethylidene tri-bromo-lactate.* [158°]. Formed by heating bromal hydrate with H_2SO_4; or by warming a mixture of bromal and tri-bromo-lactic acid (Wallach, *A.* 193, 1; Wallach a. Reinecke, *B.* 10, 2128). Monoclinic crystals, insol. water, sol. ether. Decomposed by alcohol.

BROMANIL is TETRA-BROMO-QUINONE (*q. v.*).

BROMATES AND PERBROMATES.—Salts of bromic and perbromic acids; *v.* BROMINE, OXYACIDS OF.

BROMHYDRIC ACID. HBr. (*Hydrobromic acid. Hydrogen bromide.*) Mol. w. 80·75. [−73°]. (−69°) (Faraday, *T.* 1823. 189). V. D. 39·1. S. (−25° to 0° at 760 mm.) about 690; S. (−25° to 0° at ·2 mm.) about 345 (Roozeboom, *R. T. C.* 4, 102). H. F. [H,Br] = 8,440; [H,Br,Aq] = 28,376; [H,BrAq] = 27,837 (*Th.* 2, 29). $\frac{A-1}{d}$ × At. wt. = 20·6 (Gladstone, *T.* 1870. 9).

H and Br do not combine at ordinary temperatures even in direct sunlight.

Formation.—1. By burning H charged with Br vapour.—2. By passing a mixture of H and Br over hot Pt; for details of method *v.* Harding, *B.* 14, 2085.—3. By the action of electric sparks on H and Br.—4. By the action of Br on H_2O, more quickly in presence of oxidisable bodies such as P, S, As, or lower oxides of these elements.—5. By passing H_2O and Br through a hot tube (Bourson, *C. R.* 13, 1154).—6. By passing H_2S into Br and H_2O (Naumann, *B.* 9, 1577).—7. By passing HI into Br (Hautefeuille, *C. R.* 64, 705).—8. By the mutual action of Na_2SO_3 (Mène, *C. R.* 28, 478), or $Na_2S_2O_3$ (Gladstone, *P. M.* [3] 35, 345), Br, and H_2O;

$$(Na_2SO_3Aq + H_2O + Br_2 = Na_2SO_4Aq + 2HBrAq; Na_2S_2O_3Aq + H_2O + Br_2 = Na_2SO_4Aq + S + 2HBrAq).$$

9. By leading Br into melted paraffin at 185° (Champion a. Pellet, *C. R.* 70, 620).

Preparation.—1. When small quantities are required, HBr may be prepared by the action of P and Br on H_2O ($4H_2O + P + 5Br = H_3PO_4 + 5HBr$). A glass tube is bent 3 times at about a right angle; a little Br is placed in one bend and a few pieces of P in the other; pieces of glass moistened with a very little water are placed in the limb of the tube above the P; a cork with delivery tube is fitted into the open end of the tube above the glass, and the other end of the

tube is closed by a cork. The Br is then *very gently* warmed; the reaction occurs when the Br vapour reaches the moist P, and the HBr passes off through the delivery tube.—2. When larger quantities of HBr are required it is advisable to use amorphous P. In a flask fitted with a cork carrying an exit tube and a small stoppered separating funnel, is placed 1 part amorphous P mixed with some dry sand, the P is moistened and then covered with a layer of dry sand (Linnemann, *A.* 161, 198 *note*); the exit tube is connected with a U tube nearly filled with glass beads moistened with conc. HBrAq and pieces of ordinary P (any Br which may come over is converted into HBr in this tube); this is followed by a drying tube containing $CaCl_2$ or P_2O_5, and from this a delivery tube passes into a dry cylinder filled with dry Hg standing in a Hg trough. Ten parts of Br are placed in the separating funnel and allowed to drop slowly into the flask; HBr is evolved. Towards the close of the operation the flask is gently warmed. If it is desired to prepare an aqueous solution of HBr, the U tube is fitted with an exit tube passing into the tubulus of a retort placed vertically and arranged so that the beak dips a little way under the surface of water in a bottle; should the flow of HBr slacken, the water rises into the body of the retort but cannot flow back into the generating vessel.—3. By the action of *con.* H_3PO_4Aq on KBr; 1 part KBr, 1 part H_3PO_4, and 3 parts H_2O being used (Bertrand, *C. R.* 82, 96).—4. By decomposing the bromide of an alkaline earth metal by H_2SO_4Aq; Bertrand (*l.c.*) employs two parts $CaBr_2$, 2 parts conc. H_2SO_4, and 1 part H_2O. If an alkali bromide is used, the HBr contains much Br and some SO_2.—5. An aqueous solution of HBr may be obtained by *slowly* adding P in small pieces to Br mixed with a considerable quantity of water in a vessel surrounded by ice, then adding a little more Br and then a few pieces of P (repeating if a strong solution is required), and distilling from H_3PO_4Aq (*v.* Topsöe, *B.* 3, 400).

Properties. HBr is a colourless gas, with pungent, acid, very irritating, odour; excites inflammation when applied to the skin; fumes in moist air; dissolves very largely in water; (*v. infra*) is absorbed by, and melts, ice; at $-73°$ liquefies, and then crystallises. Melsens (*C. R.* 77, 781) obtained liquid HBr by saturating wood charcoal with the gas (15,500 gram-units of heat are produced for every 81 grams HBr absorbed, Favre, *A. Ch.* [5] 1, 209), placing the charcoal in one end of a closed glass tube bent to an obtuse angle, the other end of which was well cooled, and heating the charcoal in a water bath. An aqueous solution of HBr forms a colourless, strongly acid liquid; the affinity is a very little less than that of HClAq *v.* AFFINITY.

The conc solution fumes in, but is not decomposed by exposure to, air. S.G. of solution saturated at $0° = 1{\cdot}78$; 1 c.c. contains 1·46 grams HBr (= 82·02 p.c. HBr by weight) which almost agrees with the composition calculated from the formula $HBr.H_2O$ (Bineau, *A.* 44, 237). Roozeboom (*R. T. C.* 5, 363) has obtained the hydrate $HBr.H_2O$ as a solid at low temperatures and under a pressure of 3 atmos. If conc. HBrAq is distilled at 760 mm. pressure HBr is evolved, if HBrAq containing less than 47 p.c. HBr is distilled at 760 mm. H_2O is evolved, in each case the B. P. becomes constant at 126° and the solution contains 47·38 – 47·86 p.c. HBr; the composition of this liquid is almost exactly that expressed by the formula $HBr.5H_2O$ (V. D. = 11·1 agreeing with V. D. calculated for $HBr + 5H_2O$); but it is not probable that the liquid consists of a true hydrate, as the composition varies with the pressure; thus if the pressure is 1,952 mm. the constant B. P. is 153° and the liquid contains 46·3 p.c. HBr (*v.* Roscoe, *A.* 116, 203). If dry air is passed through HBrAq at a constant temperature, either HBr or H_2O is removed, and the composition becomes constant; at 16° the liquid finally contains 51·65, and at 100° 49·35, p.c. HBr (Roscoe, *l.c.*). The S.G. and p.c. composition of HBrAq are given in the following tables (Topsöe, *B.* 3, 401; Wright, *C. N.* 23, 212).

Temp.	S.G.	P.c. HBr.	Temp.	S.G.	P.c. HBr.
14°	1·055	7·67	13°	1·302	33·84
14	1·075	10·19	13	1·335	36·67
14	1·089	11·91	13	1·349	37·86
14	1·097	12·96	13	1·368	39·13
14	1·118	15·37	13	1·419	43·12
14	1·131	16·92	13	1·431	43·99
14	1·164	20·65	13	1·438	44·02
13	1·200	24·35	14	1·451	45·45
13	1·232	27·62	13	1·460	46·09
13	1·253	29·68	14	1·485	47·87
			14	1·490	48·17

S.G.	Temp. 14° (Wright) P.c. HBr.
1·080	10·4
1·190	23·5
1·248	30·0
1·385	40·8
1·475	48·5
1·515	49·8

Reactions.—1. Not decomposed by *heat* alone, even at 700 (Hautefeuille, *C. R.* 64, 705).—2. Decomposed by heating with many *metals*, *e.g.* K, Na, Na amalgam, Sn, &c. with formation of metallic bromide and H.—3. *Chlorine* forms HCl and Br.—4. Conc. *nitric* or *sulphuric acid* forms Br, H_2O, and NO_2 or SO_2.—5. *Lead* or *silver oxide* forms metallic bromide and H_2O at ordinary temperatures; most of the *other metallic oxides* decompose HBr in a similar way on warming.—6. *Metallic peroxides*, and *acids containing metals* (*e.g.* $HSbO_3$), form metallic bromides and Br.—7. *Aqueous solution of HBr* is decomposed by most *metals* with formation of metallic bromide and H; most *metallic oxides* dissolve in HBrAq forming bromides. The heat of neutralisation of HBrAq by MOHAq or $M(OH)_2Aq$, when M = an alkali or alkaline earth metal, is the same as the heat of neutralisation of HClAq viz. 13,750; but the quantity of heat produced by the action of HBrAq on the hydrated oxides of Pt and Au, and on HgO, is much greater than the quantity of heat produced by the action of HClAq on the same compounds; the differences are

for AuO_3H_3 13,810
„ PtO_2H_2 11,890
„ PtO_4H_4 16,300
„ HgO 12,290.

The action of HBrAq on these hydrated oxides is very different from the action of the same

acid on the hydrated oxides of K, Ca, Mg, &c.; in the former cases there is little doubt that acids of the form H_2HgBr_4, H_2PtBr_4, H_2PtBr_6, and $HAuBr_4$ are formed in the solutions (v. Thomsen, *Th.* 3, 538). Many double bromides of Au, Hg, and Pt—*e.g.* $PtBr_4.2KBr$—are rather to be regarded as alkali salts of these acids than as double salts (*v. Th.* 3, 417; also GOLD, MERCURY, PALLADIUM, PLATINUM).—8. HBrAq is decomposed by *bromic acid solution*;

$HBrO_3Aq + 5HBrAq = 3H_2OAq + 6BrAq.$—

9. Conc. *sulphuric acid* heated with HBrAq forms H_2O, SO_2, and Br; dilute H_2SO_4Aq does not decompose HBrAq at ordinary temperatures. 10. *Chlorine* sets free Br from HBrAq.—11. HBrAq is partly decomposed by *potassium permanganate* solution in the cold, quickly and completely on heating.—12. By *electrolysis* of HBrAq, $HBrO_3Aq$ is produced (Riche, *C. R.* 46, 348).—13. *Bromine* dissolves in HBrAq forming a dark-coloured liquid.

Combinations.—1. With *ammonia* and *phosphine*; Ogier (*C. R.* 89, 705) gives the thermal data, $[NH^3,HBr] = 45,600$; $[PH^3,HBr] = 23,000$; using gaseous constituents and forming solid MH_4Br. 2. With *water* probably to form the hydrate $HBr.H_2O$ (*v. Properties*). The heats of solution and dilution of HBr have been measured by Thomsen (*Th.* 3, 13 and 72); the results indicate the existence in the solution of the hydrate $HBr.H_2O$, but do not suggest the formation of any other definite hydrate on dilution. The heat of dilution appears to be a continuous hyperbolic function of the quantity of water added, provided the composition of the acid to start with is $HBr.H_2O$; the results cannot, however, be expressed by quite so simple a formula, involving a single constant, as is applicable in the case of chlorhydric acid (*q. v.*). It is quite possible that the reactions of HBrAq are the reactions of the acid $HBr.H_2O$ (? = $H_2Br.OH$), and that HBr itself is not an acid (*v.* Presidential Address to Section B. by Prof. Armstrong, B. A. Meeting, 1885). Berthelot (*Bl.* [2] 19, 385; *C. R.* 61, 114; 66, 712) thinks that HBrAq contains a number of hydrates, some partially dissociated, and also the compound HBr (*v.* CHLORHYDRIC ACID). Roozeboom (*R. T. C.* 4, 108, 331; 5, 351, 363; also Van't Hoff, *ibid.* 4, 411) has determined the relations between vapour-pressure and temperature of solutions of hydrated HBr. M. M. P. M.

BROMIC ACID $HBrO_3$ *v.* BROMINE, OXY-ACIDS OF.

BROMIDES. Binary compounds of Br with more positive elements *i.e.* with any element except F, Cl, or O. Br forms binary compounds with most of the elements. The greater number may be produced by direct combination. The formation of metallic bromides is usually accompanied with production of much heat; thus, $[K^2,Br^2] = 190,620$; $[Ca, Br^2] = 140,850$; $[Zn, Br^2] = 75,930$; $[Hg, Br^2] = 50,550$; $[Au, Br^3]$ 8,850. (Liquid Br was used.) Some metallic bromides are formed by the action of Br on the oxides; *e.g.* AgBr by Br on Ag_2O. Alkalis and alkaline earths in aqueous solutions are decomposed by Br, giving bromides and bromates; certain metallic salts, in aqueous solutions, form bromides and peroxides; *e.g.* salts of Mn, Ni, Co, and Pb. Metallic iodides are decomposed wholly or in part by Br, giving metallic bromides and free I. Many metallic chlorides are partly decomposed when heated in closed tubes to about 300° with equivalent quantities of Br; after a time equilibrium is established in the system consisting of chloride, bromide, Cl, and Br; this equilibrium is not overthrown by increasing the mass of Br, the temperature, or the time (Potilitzin, *B.* 14, 1044; 15, 918; 16, 3051). Metallic bromides are usually formed by the action of HBrAq on the oxides (comp. BROMHYDRIC ACID; *Reactions*, No. 7). Most metallic bromides are white; they are generally isomorphous with the corresponding chlorides; most of them are not decomposed by heat alone, but some, *e.g.* those of Au and Pt, give up all their Br when heated. Some metallic bromides are decomposed by H_2O, *e.g.* those of Bi and Sb; others are decomposed when their aqueous solutions are evaporated, *e.g.* $AlBr_3$; most are decomposed by heating in air in presence of steam. Metallic bromides are decomposed by certain peroxides and oxidising agents, *e.g.* MnO_2, $K_2Mn_2O_8Aq$, $K_2Cr_2O_7Aq$, HNO_3Aq, with separation of Br; conc. H_2SO_4Aq sets free a little HBr, but decomposes most of the bromides to sulphate and Br with simultaneous formation of SO_2; HCl and HClAq form HBr and metallic chloride. When a metallic bromide is heated with solid $K_2Cr_2O_7$ and conc. H_2SO_4, free Br is obtained (distinction from chlorides). Aqueous solutions of alkali bromides dissolve large quantities of Br, probably with formation of perbromides in solution; Berthelot (*C. R.* 91, 195 and 706) gives the numbers (using gaseous Br) $[KBrAq, Br^2] = 11,500$. Aqueous solutions of alkali, alkaline earth, and magnesian bromides partly decompose AgCl when the salts are shaken together for a few minutes at the ordinary temperature; the percentage of AgBr formed varies from 95 when LiBrAq is used, to 81·8 when $CdBr_2Aq$ is employed (Potilitzin, *B.* 18, 1522). The binary compounds of Br with the non-metals are fairly stable bodies; they are usually produced by direct combination. Bromides of B, P, C, and Si are stable as gases. Br forms definite, stable, compounds only with the more metallic and positive members of the oxygen group of elements; bromides of Te are gasifiable, Se_2Br_2 is fairly stable, but is decomposed by heat, S_2Br_2 is a feebly-marked body, and no oxide of Br is known. Bromide of iodine is a fairly well marked compound, $[I, Br] = 2,500$ (Berthelot, *C. R.* 90, 841; using liquid Br and solid I). Bromine chloride is very easily decomposed, and no compound of Br and F is definitely known. If N bromide exists it is extremely unstable (*v.* also HALOGEN ELEMENTS, BINARY COMPOUNDS OF: for the individual bromides *v.* the articles on the various elements.)

M. M. P. M.

BROMIDES, ORGANIC *v.* BROMINE, ORGANIC COMPOUNDS OF.

BROMINE. Br. At. w. 79·75. Mol. w. 159·50. [−24·5°] (Baumhauer, *B.* 4, 927), [−7·2°] (Philipp, *B.* 12, 1424; according to Philipp, the lower M.P. was due to presence of Cl). [−7·05°] (Ramsay a. Young, *C. J.* 49, 453); (63°) (Pierre, *A. Ch.* [3] 20, 5); (59·27°) (Thorpe, *C. J.* 37, 172); (58·7°) (Ramsay a. Young, *l.c.*). S.G. $\frac{0}{0}$ 3·1872 (Pierre, *l.c.*); $\frac{0}{4}$ 3·18828 (Thorpe,

l.c.). S.G. at B.P. 2·9822 (Thorpe, *l.c.*). V.D. 80 (*v.* p. 536, *Properties*). S.H. (solid −78° to −20°) ·08432 (Regnault, *A. Ch.* [3] 26, 286). S.H. (liquid 13° to 45°) ·1071 (Andrews, *C. J.* 1, 18). S.H.p. (equal mass of H_2O = 1) (83°–228°) ·05552 (Regnault, *Acad.* 26, 1): S.H.v. (equal mass of H_2O = 1) ·0429; (equal volume of air = 1) 1·395 (Clausius, *Mechan. Wärmetheorie*, 1, 62 [1876]). $\frac{\text{S.H.p.}}{\text{S.H.v.}}$: (20°–388°) 1·293 (Strecker, *W.* 13, 20; experimentally determined). Expansion (0° to B.P.) V = $1 + \cdot 0010621t + \cdot 0000018771t^2 - \cdot 0000000030853t^3$ (Thorpe, *l.c.*). S. (5°) 3·68, (10°) 3·327, (15°) 3·226, (20°) 3·208, (25°) 3·167, (30°) 3·126, (Dancer, *C. J.* 15, 477). Heat of fusion = 16,185, Regnault (*A. Ch.* [3] 26, 268). $\frac{A-1}{d}$ × At. wt. = 16·23 (Gladstone, *T.* 1870. 9). Emission-spectrum; marked lines are 3980, 6356, and lines beginning with 6999 (Salet, *A. Ch.* [4] 28, 26). Absorption-spectrum characterised by many bands between 6801·5 in the red and 5244·1 in the green (Roscoe a. Thorpe, *T.* 1877. 207).

Bromine was discovered by Balard in 1826 (*B. J.* 7, 102); it was previously obtained by Liebig, but supposed by him to be iodine chloride (*v.* Hofman's *Life Work of Liebig*); and by Joss, but regarded by him as selenium (*J. pr.* 1, 129).

Occurrence. Never free; widely distributed, but not in large quantities, chiefly in combination with K, Na, and Mg. In sea water (for quantities, *v.* Berglund, *B.* 18, 2888), sea-weed, saline springs, and many marine plants and animals (Kundt a. Wöhler, *P.* 10, 509; Strohmeyer, *S.* 49, 249; Hembstädt, *B. J.* 7, 110). According to Marchand (*C. R.* 31, 495) all waters, including rain and snow, contain traces of bromides. In various minerals, chiefly as AgBr in Mexico and Chili (Berthier, *A. Ch.* 77, 417; 79, 161); in minute quantities in Silesian zinc ores (Hollunder, *B. J.* 8, 82); in Chili saltpetre (Grüneberg, *J. pr.* 60, 172); &c., &c.

Preparation. The starting-point is the concentrated liquor of certain saline springs, the residual liquor obtained in working the salt deposits at Stassfurt, or the solution of the ash of sea plants. The liquid is freed from the less soluble salts, chiefly chlorides and sulphates, by concentration and crystallisation, mixed with MnO_2 and HClAq, and distilled. The quantities of the reacting materials are arranged so that there is always an excess of bromide, in order to prevent formation of bromine chloride (*v.* Mohr, *A.* 22, 66). In some cases the concentrated liquor is heated with H_2SO_4Aq, sulphates are then removed by crystallisation, and the mother liquor is distilled with MnO_2 and H_2SO_4Aq (*v.* Herrmann, *P.* 13, 175; 14, 613). The Br is condensed in water and converted into NaBr and $NaBrO_3$ by treatment with NaOHAq, the liquid is evaporated to dryness, the residue heated to decompose $NaBrO_3$, and the NaBr is decomposed by pure MnO_2 and H_2SO_4Aq. Iodine may be removed from the original liquor, before decomposing by MnO_2 and acid, by the action of Cl, or by ppg. as Cu_2I_2 (Bussy, *B. J.* 18, 117; Balard, *B. J.* 7, 102). Chlorine may be removed by decomposing the distillate from the first action of MnO_2 and acid by BaOAq, evaporating to dryness and heating, dissolving out $BaBr_2$ in alcohol, filtering from insoluble $BaCl_2$, evaporating to dryness, and decomposing by MnO_2 and H_2SO_4Aq (Piria, *B. J.* 19, 277). Adrian (*J.* 1870. 248) removes Cl by washing the distillate with water and small successive quantities of ether; he then digests with starch paste to remove I, and again distils. Stas (*Fr.* 25, 213) frees from I and Cl by dissolving in KBrAq, adding ZnO and distilling. Cyanogen is occasionally found in samples of Br; it may be detected by conversion into $K_4Fe(CN)_6$ by digesting with iron filings, and rapidly filtering (Phipson, *C. N.* 28, 51). Bromoform is another impurity; it is detected by its odour, after addition of KIAq sufficient to convert all the Br into KBr, and removal of the I by the action of $Na_2S_2O_3$Aq (Reymann, *B.* 8, 790). Bromine is prepared from laboratory residues containing Br compounds by making alkaline with KOHAq, and distillation with solid $K_2Cr_2O_7$ and excess of H_2SO_4Aq (2 parts strong acid to 1 part water by weight) added gradually through a funnel tube (Bolas a. Groves, *C. J.* [2] 9, 784). To prepare pure Br for atomic weight determination, Stas removed I from commercial KBr by dissolving in water, adding BrAq to ⅓ of the liquid till the I which at first separated redissolved forming a clear orange-yellow coloured liquid, adding the other ⅔ of the liquid and shaking repeatedly with pure CS_2. The liquid was then warmed to remove all CS_2; the KBr was oxidised to $KBrO_3$ by the action of Cl in presence of pure KOHAq (for details *v.* Stas, *Nouv. R.* 159; or pp. 159–160 of Aronstein's German translation *Untersuchungen über die Gesetze der chem. Proportionen*, &c.); the $KBrO_3$ was purified by repeated crystallisation, and a part of it was converted back to KBr by heating in a porcelain vessel in small successive quantities. By decomposing a mixture of KBr and $KBrO_3$ (in the ratio 5KBr : $KBrO_3$) with pure H_2SO_4Aq, Br was obtained. A portion of this Br was then digested with milk of lime and NH_4Aq, whereby $CaBr_2$Aq was obtained; this liquid was saturated with another portion of the purified Br; water was added to pp. Br; the ppd. Br was separated, and digested several times with pure dry $CaBr_2$ (prepared by the action of part of the purified Br on CaO); the Br was then shaken in contact with pure P_2O_5, then allowed to remain in contact for 12 hours with pure BaO which had been strongly heated, and finally poured off and distilled. All operations were conducted in apparatus made wholly of glass.

Properties. — At ordinary temperatures a dark brown red volatile liquid with most irritating odour (βρῶμος = stench); in thick layers almost black; vapour is yellowish red, and becomes less transparent as temperature is increased (*v.* Andrews, *B. A.* 1871. (Sec.) 66); solidifies to a grey-brown crystalline mass with semi-metallic lustre. Very poisonous. Vapour acts on mucous membrane and causes violent irritation. Non-conductor of electricity; but an aqueous solution of Br is a better conductor than pure water (such a solution contains some HBr) (Balard, *A. Ch.* [2] 32, 371; De la Rive, *B. J.* 8, 83; Solly, *A.* 20, 124). Dissolves

sparingly in water (*v. supra*); solutions of *x* parts Br by weight in 1,000 parts H_2O have following S.G. (Slessor, *J.* 1858. 100):—

x.	S.G.	*x.*	S.G.	*x.*	S.G.
10·7	1·009	12·3	1·0122	20·9	1·018
11·7	1·0093	18·7	1·0149	31–31·7	1·0236
12·0	1·0099	19·5	1·0158		

Solution in water is attended with production of heat $[Br^2,Aq] = 1080$ (*Th.* 2, 25); solution is pale orange-yellow. Dissolves more readily in alcohol, and in all proportions in ether, CS_2, and $CHCl_3$; solution is accompanied by chemical change; soluble also in conc. aqueous solutions of KBr and many other metallic bromides, frequently with formation of perbromides; also in conc. HClAq and HBrAq, and in liquid SO_2 (Sestini, *Z.* 1868. 718). Br is absorbed by wood charcoal with considerable rise of temperature (Melsens, *C. R.* 77, 781). In presence of H_2O, acts as a bleacher and disinfectant.

The atomic weight of Br has been determined (1) by analyses, and determinations of V. D., of many gaseous compounds, *e.g.* BrH, Br_2Cd, Br_4B, Br_4Sn, &c.; (2) by determination of S. H. of solid Br; (3) by comparison of bromides &c. with isomorphous chlorides and iodides &c.; (4) by syntheses of AgBr by Marignac (*B. J.* 24, 193); by syntheses of AgBr by Stas (*Nouv. R.* 158, 171); by reduction of $AgBrO_3$ by Stas (*Nouv. R.* 199); by conversion of KBr to AgBr by Stas (*l.c.* 303); by conversion of AgBr to AgCl by Dumas (*A. Ch.* [3] 55, 162). In gaseous molecules containing Br the atom of Br is monovalent. Br acts as a strongly negative non-metallic element; it combines directly with most metals forming salts; its compounds with non-metals one of which is H are acids. The substitution of H by Br in carbon acids seems to increase the relative affinity of the acids (*v.* AFFINITY, p. 83); generally speaking, the introduction of Br in place of H in carbon compounds is accompanied by the production of more or less acidic properties.

In its chemical relations Br stands between Cl and I; the heat of formation, in solution, of a metallic bromide is usually about *n* 11,000 gram-units less than that of the chloride, and about *n* 26,000 gram-units more than that of the iodide, of the same metal, where *n* is a whole number, usually 1, 2, 3, or 4; metallic bromides are wholly or partly decomposed by Cl, and metallic iodides by Br; metallic chlorides are partially decomposed by Br (*v. Reactions*, No. 12). The relative affinities of the acids HCl, HBr, and HI in aqueous solution are, however, nearly the same (*v.* AFFINITY, p. 77). In its compounds, Br appears to be positive to Cl, F, and O. No oxide of Br is at present known; the oxyacids of Br exist only in presence of water; they are much less stable than the oxyacids of iodine: one of the oxyacids of Cl ($HClO_4$) has been obtained in separate and definite forms, although it is an extremely unstable compound; oxides of Cl are known as gases, and an oxide of I (I_2O_5) exists as a solid body. No oxide or oxyacid of F is known (*v.* BROMIDES, HALOGEN ELEMENTS, and HALOGEN ELEMENTS, BINARY COMPOUNDS OF).

The S.G. of Br gas at 99° was found by Mitscherlich to be 5·54 (air = 1) and by Meyer a. Züblin to be 5·38 at 100°: the S.G., calculated on the assumption that $2 \times 79{\cdot}75 = 159{\cdot}50$ parts by weight of Br occupy 2 volumes, is 5·51. At very high temperatures (approximately 1570°) the S.G. is less than the calculated; Meyer a. Züblin (*B.* 13, 405) obtained values lying between those calculated from the formulæ Br_2 and $\frac{2}{3}Br_2$; when the Br was obtained by decomposing $PtBr_4$ at high temperatures the S.G. at 1570° nearly agreed with that calculated for $\frac{2}{3}Br_2$ (3·66). The S.G. of Br vapour diluted with 10 volumes air, at 50° under the B.P. of Br, was determined by Langer a. Meyer to be 5·52 (*B.* 15, 2769). Jahn's determinations (*B.* 15, 1238) show that bromine does not attain the S.G. calculated for Br_2 until it is heated about 160° above its B.P.; the deviations are small; the S.G. at any temperature up to about 220° may be approximately found by the formula S.G. $= a + bt$, where $a = 5{\cdot}8691$ and $b = -{\cdot}00153$. (For S.G. of Cl and I gases *v.* these elements; *v.* also HALOGEN ELEMENTS.)

Reactions.—1. Br dissolves in *water* with production of heat $[Br^2, Aq] = 1080$ (*Th.* [2] 25); the water is slowly decomposed, more quickly in direct sunlight, with formation of HBr and O. Bromine water, therefore, acts as an oxidiser; *e.g.* HNO_2Aq is oxidised to HNO_3Aq (Schönbein, *J. pr.* 37, 144), $Mn(C_2H_3O_2)_2Aq$ to MnO_2 (Kämmerer, *B.* 4, 218); sugar, mannite, benzene, &c., &c., to various oxidised derivatives (Blomstrand, *A.* 123, 248). If NO is led into Br cooled below 0° the gas is absorbed, and on adding water HBr and higher oxides of N are formed (Landolt, *A.* 116, 177).—2. *Steam* mixed with Br and passed through a red-hot tube yields HBr and O.—3. *Hydrogen peroxide* evolves O, and HBr is formed (Schönbein, *A.* 108, 169).—4. Aqueous solutions of *potash* or *soda* are decomposed by Br forming KBrAq (or NaBrAq) and $KBrO_3Aq$ (or $NaBrO_3Aq$): CaO and BaO form bromides and O.—5. Aqueous *ammonia* yields NH_4BrAq and N.—6. *Urea* is decomposed by BrAq with evolution of N.—7. *Hydriodic acid* and *iodides* in solutions are decomposed by Br with formation of HBrAq, or MBrAq, and I.—8. *Sulphuretted hydrogen* yields HBr, and S which partly combines to form S_2Br_2; this decomposition proceeds either in presence or absence of water (Naumann, *B.* 9, 1574).—9. In contact with excess of *silver nitrate solution*, AgBr and HBrOAq are produced (Spiller, *J.* 1859. 67).—10. With *carbon disulphide*, crystalline $C_2S_2Br_4$ is formed (Hell a. Urech, *B.* 15, 987). 11. *Carbon compounds* are usually acted on by Br; sometimes H is withdrawn, sometimes this is accompanied by substitution of Br, and sometimes more complete decomposition results.—12. Br partly decomposes *metallic chlorides* when heated in equivalent quantities to 270°–300°; if the mass of Br is increased, the amount of decomposition increases up to a limit which is not passed by increasing the mass of Br, the temperature, or the time of action (Potilitzin, *B.* 14, 1044; 15, 918; 16, 3051). According to Humpidge (*B.* 17, 1838) AgCl is partly decomposed by contact with water and an equivalent quantity of Br; thus 5·2 p. c. Cl was removed from AgCl after 24 hours' action at 11°, and 14·53 p. c. after 12 hours' action at 44°.

Combinations.—1. With *water* at 4° forming red octahedral crystals of $Br.10H_2O$ which are

decomposed to Br and H_2O at 15° (Löwig, *P.* 14, 114; 16, 375). For dissociation-pressures *v.* Roozeboom (*R. T. C.* 4, 65).—2. Combines directly with most of the *elements*, especially the *metals*, often with production of much heat and sometimes light (*v.* BROMIDES). Does not combine directly with C or O. According to Merz a. Weith (*B.* 6, 1518) dry Br and Na do not combine even at 200°. Combines with liquid Cl at −90° (Donny a. Mareska, *C. R.* 20, 817). No oxide of Br is at present known.

Detection.—The physical properties of Br enable this body to be easily detected when uncombined. Bromides are decomposed by ClAq, giving Br and chloride of the metal. Solution of N_2O_3 in conc. H_2SO_4Aq does not decompose bromides, but does decompose iodides with production of I; on this reaction is based a method for detecting bromides in presence of iodides. Solid bromides are decomposed by heating with $K_2Cr_2O_7$ and conc. H_2SO_4Aq, with formation of Br; chlorides yield CrO_2Cl_2.

Estimation.—Free Br may be estimated volumetrically by measuring the I set free by it from KIAq, or by finding the mass of As_2O_3 which it oxidises to As_2O_5 in an alkaline solution; Br may also be combined with H to form HBrAq, by treatment with H_2S, or SO_2, in aqueous solutions; the HBr may then be estimated by pp. with $AgNO_3Aq$. Br in bromides is usually estimated as AgBr, pp. being accomplished by addition of $AgNO_3Aq$; insoluble bromides may be fused with Na_2CO_3, dissolved, and acidulated with HNO_3Aq. In presence of chlorides, or iodides, Br in bromides must be determined by *indirect* methods (*v.* Manuals of Analysis).

Bromine, Chloride of. BrCl. Mol. w. unknown. Chlorine is absorbed by Br with formation of a red yellow, mobile, very volatile, liquid, which gives off a dark yellow, very irritating, vapour with strong bleaching properties; many metals burn in this vapour to chloride and bromide (Balard, *A. Ch.* [2] 32, 371). If the Br is cooled to 0° the liquid finally contains Br and Cl in the proportion BrCl; at ordinary temperatures less Cl than is required by the composition BrCl is absorbed (Bornemann, *A.* 189, 183). At temperatures above +10° the compound BrCl decomposes with evolution of Cl. By adding a little H_2O to BrCl, and cooling to 0°, yellow-brown crystals of $BrCl.10H_2O$ separate (Bornemann, *l.c.*); these melt at 7°, and are decomposed by NH_3 to N, NH_4Br, and N chloride (Löwig, *Das Brom und seine chemischen Verhältnisse*; Heidelberg, 1829, p. 64). An aqueous solution of BrCl, obtained by dissolving Br in ClAq, is decomposed by alkalis giving alkali bromate and chloride; in sunlight $HBrO_3Aq$ and HClAq are formed; reducing agents, *e.g.* SO_2Aq, Zn powder, Fe filings, P, NO, &c., withdraw Cl, and set Br free (Schönbein, *J. pr.* 88, 483).

Bromine, Cyanide of: better called **Cyanogen Bromide**. Obtained by action of Br on $Hg(CN)_2$, KCN, or HCN; *v.* CYANIC ACIDS, vol. ii. p. 313.

Bromine, Hydrate of. $Br.10H_2O$. Obtained by cooling a saturated solution of Br in H_2O; *v.* BROMINE; *Combinations*, No. 1.

Bromine, Iodide of: better called **Bromide of Iodine**; *v.* IODINE.

Bromine, Oxyacids of. No oxide of Br is known. The acids HBrO and $HBrO_3$ exist in aqueous solutions only; both solutions are decomposed on heating, HBrOAq even at 30°. Perbromic acid, $HBrO_4$, was said by Kämmerer to be produced by the action of Br gas on $HClO_4Aq$ (*J. pr.* 90, 190); but later experiments have shown that this acid has not yet been obtained (*v.* Pattison Muir, *C. J.* 30, 469; MacIvor, *C. N.* 33, 35; Wolfram, *A.* 198, 95). BrAq is not oxidised by such reagents as $K_2Mn_2O_8Aq$, $K_2Cr_2O_7Aq$, HNO_3Aq, or HClOAq; but the action of $HClO_3Aq$ or $HClO_4Aq$ produces $HBrO_3Aq$. Dilute solutions of HBrO and $HBrO_3$ are also formed by electrolysing HBrAq, MBrAq, or BrAq; also by the action of metallic oxides on BrAq. No salts of HBrO are known except in aqueous solutions; salts of $HBrO_3$ exist as solids, they are all easily decomposed by heat with evolution of O, and frequently also of Br. The addition of O to KBrAq would be attended by disappearance of much heat; Thomsen gives these numbers $[KBrAq, O^3]$ 15,930; also $[Br^2, O, Aq] = -16{,}200$. The following data show that the heat of formation of the oxyacids of Br is less than that of HBr, and is also less the more O the acid contains:—$[H, Br, Aq] = 28{,}380$; $[H, Br, O, Aq] = 26{,}080$; $[H, Br, O^3, Aq] = 12{,}120$ (*Th.* 2, 400). These data are analogous with those for the corresponding compounds of Cl, but differ from the data for the similar compounds of I (*v.* HALOGEN ELEMENTS).

I. HYPOBROMOUS ACID, AND HYPOBROMITES. HBrOAq and MBrOAq. Gay Lussac obtained a gas by the action of Br on dry HgO and supposed it to be an oxide of Br; Pelouze, and more recently Dancer (*C. J.* 15, 477), proved that only O is thus produced. An aqueous solution of HBrO is obtained by the action of BrAq on the oxide, or nitrate, of Hg, or Ag; Hg_2O and PbO do not oxidise BrAq (Spiller, *C. N.* 6, 249).

Formation. By the action of BrAq on HgO—repeating several times—Hg_2OBr_2, HBrOAq, and $HgBr_2Aq$ are formed; by distilling *in vacuo*, a liquid containing 6·2 p.c. Br as HBrO is obtained, but it cannot be quite freed from $HgBr_2$ (Balard, *A. Ch.* 32, 337).

Preparation.—Pure BrAq is shaken with excess of $AgNO_3Aq$ until the colour and odour of Br have gone; the straw-coloured liquid is then at once distilled *in vacuo*; at 50 mm. pressure it boils at 40°. The distillate gets richer in HBrO until ·736 p.c. Br is present as HBrO (then it gets poorer in the acid); about 46½ p.c. of the Br used is changed to HBrO.

Properties and Reactions. Solution with 6·2 p.c. Br as HBrO decomposes at 30° giving Br and $HBrO_3Aq$; solution with ·736 Br as HBrO decomposes, into the same products, at 60°. HBrOAq is a strongly bleaching liquid; it is decomposed by Ag_2O (and slowly by contact with $AgNO_3Aq$) with formation of O and AgBr, by H_2O_2Aq with evolution of O; and by HClAq, HBrAq, and HIAq, with formation of Br (Schönbein, *J. pr.* 88, 475).

No **hypobromites** have been obtained except in dilute aqueous solutions. By the action of alkalis, alkali carbonates, or phosphates (Fritzsche, *A.* 40, 251), on BrAq, yellow, strongly bleaching, liquids are produced; these

liquids are very unstable, decomposing in air, quickly at 30°. They decompose urea with evolution of N; $-CON_2H_4 + 3HBrOAq = CO_2 + N_2 + 3HBrAq + 2H_2OAq$ (E. Knop, *C. C.* 1870. 132). Balard (*A. Ch.* 32, 337; *J. pr.* 4, 165) described bodies resembling bleaching powder, obtained by the action of BrAq on CaO_2H_2 and BaO_2H_2; by the addition of water and filtration, bleaching solutions were produced, very unstable, and easily decomposed, even by CO_2.

II. Bromic Acid and Bromates. $HBrO_3Aq$ and $MBrO_3$. Bromic acid, $HBrO_3$, is known only in aqueous solution.

Formation. 1. By electrolysis of HBrAq (Riche, *C. R.* 46, 348). 2. By action of heat on hypobromites in solution.

Preparation. $BaBrO_3$ is prepared by adding Br little by little to conc. BaO_2H_2Aq until the liquid is slightly red, when $BaBrO_3$ pps. and $BaBr_2$ remains in solution. The $BaBrO_3$ is crystallised from hot water, dried, and ground to fine powder; 100 parts are digested for some time in the cold or at a very gentle heat, with 24 parts conc. H_2SO_4 mixed with 240 parts H_2O; excess of H_2SO_4 is removed from the liquid by gradual addition of BaO_2H_2Aq; the acid liquid is evaporated *in vacuo* (Rammelsberg, *A.* 40, 147). Kämmerer passes Cl_2O into Br under H_2O until the colour of the Br has disappeared; $5Cl_2O + Br_2Aq + H_2O = 2HBrO_3Aq + 10ClAq$ (*J. pr.* 85, 452).

Properties and Reactions. – $HBrO_3Aq$ may be concentrated *in vacuo* until the liquid contains 50·59 p.c. $HBrO_3$; the composition then nearly agrees with the formula $HBrO_3.7H_2O$. When concentrated by heating in an open vessel decomposition begins when the liquid contains 4·27 p.c. $HBrO_3$, with production of Br, O, and H_2O. $HBrO_3Aq$ is a colourless, acid liquid, with a bromine-like smell. Oxidisable bodies decompose $HBrO_3Aq$ with separation of Br; *e.g.* $5SO_2 + 2HBrO_3Aq + 4H_2O = 5H_2SO_4Aq + Br_2Aq$; $5H_2S + 2HBrO_3Aq = 6H_2OAq + 5S + Br_2Aq$. Iodine quickly decomposes $HBrO_3Aq$, forming HIO_3 (Kämmerer, *J. pr.* 85, 452); Cl, dilute H_2SO_4Aq, and dilute HNO_3Aq, are without action. HBrAq decomposes $HBrO_3Aq$, forming H_2O and Br; HClAq and HIAq form H_2O and BrCl or IBr. The heat of neutralisation of $HBrO_3Aq$ is the same as the mean value for the stronger monobasic acids; $[HBrO^3Aq, NaOHAq] = 13{,}780$ (*Th.* 1, 240). Bromic acid is monobasic and forms one series of salts, the **bromates**, M^IBrO_3 and $M^{II}2BrO_3$; these salts are formed by the action of $HBrO_3Aq$ on the oxides, hydroxides, or carbonates, of the metals; the alkali and alkaline earth salts are also formed, always with bromides, by the action of Br on aqueous solutions of the alkali or alkaline earth hydroxides. (For special methods *v.* individual salts; also Kämmerer, *J. pr.* 85, 452.) The bromates crystallise well; they are all soluble in water; the least soluble are $AgBrO_3$ and $HgBrO_3$. They are decomposed by heat; sometimes O is evolved and metallic bromide remains, *e.g.* bromates of alkalis, Hg, and Ag; sometimes Br and O are evolved, and oxide remains, *e.g.* bromates of Mg, Al, Zn; or a mixture of oxide and bromide remains, *e.g.* bromates of Pb, Cu, &c. Dilute HNO_3Aq, H_2SO_4Aq, or H_3PO_4Aq, decomposes bromates giving $HBrO_3Aq$ most of which decomposes to Br, O, and H_2O. Solutions of bromates react similarly to solution of $HBrO_3$ towards SO_2, H_2S, HClAq, HBrAq, and HIAq. The bromates have been chiefly investigated by Rammelsberg (*A.* 40, 147; *P.* 90, 16); Löwig (*B. J.* 12, 120); and Marignac (*C. R.* 45, 650; *J.* 1857. 127). The following are the better-studied salts.

Barium bromate $Ba(BrO_3)_2.H_2O$. Prismatic, monoclinic, crystals; isomorphous with $Ba(ClO_3)_2$ (Marignac a. Rammelsberg); S. (100°) 4·2; (15°–18°) ·77. Prepared by decomposing $KBrO_3Aq$ by $Ba(C_2H_3O_2)_2Aq$.

Cadmium bromate $Cd(BrO_3)_2.H_2O$. Columnar trimetric crystals; prepared by $CdSO_4Aq + BaBrO_3Aq$. S. (15°–18°) 125. On heating, leaves CdO and $CdBr_2$ (Rammelsberg).

Calcium bromate $Ca(BrO_3)_2.H_2O$. Monoclinic plates (Marignac); prepared by $CaO_2H_2Aq + HBrO_3Aq$. S. (15°–18°) 99. Heated to 180° loses H_2O, at higher temperature gives O and $CaCl_2$ (Rammelsberg).

Cobalt bromate $Co(BrO_3)_2.6H_2O$. Transparent, hyacinth-coloured, monometric octahedra; prepared by $HBrO_3Aq + CoCO_3$, or $Ba(BrO_3)_2Aq + CoSO_4Aq$. S. (15°–18°) 45·5. Heated, gives CoO (Rammelsberg).

Copper bromate $Cu(BrO_3)_2.5H_2O$. Blue-green crystals, efflorescing over H_2SO_4 *in vacuo*; very soluble; lose H_2O completely, and a little Br also at 200°. Prepared similarly to $Co(BrO_3)_2$.

Lead bromate $Pb(BrO_3)_2.H_2O$. Small, lustrous, monoclinic prisms; isomorphous with $Sr(BrO_3)_2.H_2O$ (Rammelsberg). S. (15°–18°) 1·33. Prepared by $HBrO_3Aq + PbCO_3$, or conc. $Pb(C_2H_3O_2)_2Aq + KBrO_3Aq$. Heated over 180° gives Br, PbO_2, and $PbBr_2$, at higher temperatures gives Pb_3O_4, Br, and $PbBr_2$.

Magnesium bromate $Mg(BrO_3)_2.6H_2O$. Large, efflorescent, monometric octahedra; S. (15°–18°) 71·5; loses all H_2O above 200°. Prepared by $MgO + HBrO_3Aq$, or

$MgSiF_6Aq + KBrO_3Aq$.

Mercury bromates $Hg_2(BrO_3)_2$, and $Hg(BrO_3)_2.2H_2O$. Mercurous bromate is prepared by $Hg_2(NO_3)_2Aq + KBrO_3Aq$ or $HBrO_3Aq + Hg_2O$; mercuric bromate by $HBrO_3Aq$ + freshly ppd. HgO. Both form small white crystals; the mercurous salt forms yellow basic $Hg_2(BrO_3)_2.Hg_2O$ by the action of H_2O; when heated it decomposes with detonation (Rammelsberg). The mercuric salt decomposes at 130°–140°, with slight explosion, to HgO, $HgBr_2$, and Hg_2Br_2. S. (15°–18°) ·17, (100°) 1·6.

Nickel bromate $Ni(BrO_3)_2.6H_2O$. Prepared as, is isomorphous with, and generally resembles, the Co salt (*q. v.*). S. (15°–18°) 28. (Rammelsberg; *v.* also Marbach, *P.* 94, 412).

Potassium bromate $KBrO_3$. Prepared by adding Br, or BrCl, to conc. KOHAq; or by adding Br to K_2CO_3Aq which has been previously saturated with Cl. Rhombohedra (Rammelsberg; Marignac, *J.* 1859. 139; *v.* also for crystalline forms, Löwig, *B. J.* 12, 120; Fritzsche, *A.* 40, 251; Marbach, *P.* 94, 412). S.G. $\frac{17.5°}{17.5°}$ 3·271 (Kremers, *P.* 99, 443). S. (0°) 3·1, (20°) 6·9, (40°) 13·2, (100°) 50 (Kremers, *P.* 97, 1). Insol.

in alcohol. B. P. of saturated $KBrO_3Aq = 104°$. $KBrO_3$, when heated, melts at 350°, then begins to decompose, at first slowly, then rapidly and explosively, with evolution of O and a little Br. According to Fritzsche (*A.* 40, 251), crystals of $KBrO_3$ prepared from exactly neutral solutions, or from solutions containing a little acetic acid, decrepitate before decomposing, and lose 1·3 p.c. of their mass (chiefly water); if the resulting powder is placed in warm water, O is evolved at the surfaces of the undissolved particles, but most of the O is again absorbed by the liquid; on evaporation, pure $KBrO_3$ crystallises out. Fritzsche supposes that $KBrO_3$ is partly decomposed by heat to hypobromite and perbromate, that the latter acts on water, evolving O and forming $KBrO_3Aq$, and that the O is absorbed by the KBrOAq with formation of $KBrO_3Aq$. $KBrO_3$ is decomposed by conc. H_2SO_4Aq, with evolution of O and Br (Löwig); by HNO_3Aq, with production of KNO_3Aq, Br, and O (Penny, *A.* 37, 206). $KBrO_3Aq$ decomposes H_2S, separating S, and forming HBrAq, and H_2SO_4Aq. Heated with combustible bodies, $KBrO_3$ evolves O rapidly and explosively.

Silver bromate $AgBrO_3$. Dimetric prisms (Marignac). Prepared by $AgNO_3Aq + HBrO_3Aq$ or $KBrO_3Aq$, and crystallising from hot water. Stable in air free from organic matter. Decomposes on heating.

Sodium bromate $NaBrO_3$. Prepared as $KBrO_3$. At 4° crystallises with xH_2O forming efflorescent needles (Löwig); above 4° the anhydrous salt separates, isomorphous with $KBrO_3$ according to Löwig (*B. J.* 12, 120). S.G. $\frac{17.5}{?}$ 3·339. S. (0°) 28, (20°) 38·5, (60°) 62·5, (100°) 99 (Kremers, *P.* 97, 1). B. P. of saturated $NaBrO_3Aq = 109°$. Decomposes when heated as $KBrO_3$ (*q. v.*).

Strontium bromate $Sr(BrO_3)_2.H_2O$. Monoclinic prisms. Is amorphous with the Ba salt (Rammelsberg). S. (15°–18°) 33. Loses H_2O at 120°. Prepared by $SrCO_3 + HBrO_3Aq$.

Zinc bromate $Zn(BrO_3)_2.6H_2O$. Monometric octahedra, isomorphous with the Mg salt; prepared as $Co(BrO_3)_2.6H_2O$. Melts at 100°; loses $6H_2O$ at 200 with partial decomposition to ZnO, Br, and O. S. (15°–18°) 100. Soluble in NH_3Aq (Rammelsberg).

Besides the foregoing, bromates of Ce, La, and Di of the form $M(BrO_3)_3.6H_2O$ have been prepared (Rammelsberg, Marignac, Hermann *J. pr.* 82, 385). Bromates of Al, Cr, Fe, and V; of Pd, and Pt; of Bi; and of Sn, seem to exist. They have, however, either not been obtained in definite form, or have been very slightly examined.

Bromine, Sulphide of: better called **Sulphur Bromide** (*v.* SULPHUR). M. M. P. M.

BROMINE, ACTION ON ORGANIC BODIES *v.* BROMO-COMPOUNDS.

BROMO-. *Use of this prefix applied to inorganic compounds*: for *bromo-compounds* and *bromo-salts* *v.* the element the bromo-compound of which is sought for, or the salts to the names of which *bromo-* is prefixed. Thus *bromochloride of carbon* will be found under CARBON; bromo-chromate of potassium under CHROMATES.

BROMO-ACENAPHTHENE *v.* ACENAPHTHENE.

BROMO-ACENAPHTHYLENE *v.* ACENAPHTHYLENE.

BROMO-ACETAL *v.* BROMO-ACETIC ALDEHYDE.

BROMO-ACETAMIDE *v.* BROMO-ACETIC ACID.

ν-**Bromo-acetamide** *v.* *Aceto-bromo-amide*, p. 5.

BROMO-ACETAMIDO- *v.* BROMO-AMIDO-.

BROMO-ACETANILIDE *v.* BROMO-ANILINE.

BROMO-ACETIC ACID $C_2H_3BrO_2$ *i.e.* $CH_2Br.CO_2H$. [51°]. (208°).

Formation.—1. By bromination of acetic acid (Perkin a. Duppa, *A.* 108, 106; Hell a. Mühlhäuser, *B.* 11, 241; 12, 735).—2. By heating ethyl acetate with bromine at 150° (Crafts, *A.* 129, 50).—3. From glycollic acid and HBr (Kekulé, *A.* 130, 11).—4. By atmospheric oxidation of an alcoholic solution of bromo-ethylene (Glöckner, *A. Suppl.* 7, 107).—5. By the action of bromine on dry glycerin (Barth, *A.* 124, 341). 6. From chloro-acetic acid and HBr (Demole, *B.* 9, 561). 7. From ethylene bromide and fuming HNO_3 (Kachler, *M.* 2, 259).

Preparation.—Br, glacial acetic acid, and some CS_2 are boiled with inverted condenser; the yield is nearly theoretical (Michael, *Am.* 5, 202).

Properties. Deliquescent rhombohedra; v. sol. water. Blisters the skin.

Reactions. 1. Heated with *zinc* it yields $Zn(OAc)_2$ and $ZnBr_2$. 2. NH_3 forms glycocoll. 3. *Silver benzoate* forms glycollide, benzoic acid and AgBr. 4. *Silver powder* at 130° forms succinic acid. 5. *Benzyl sulphide* $(C_7H_7)_2S$ forms benzyl bromide and $S(CH_2.CO_2H)_2$ (Letts, *Tr. E.* 28, 612). Allyl sulphide acts similarly.—6. Bromo-acetic acid and its ethyl salt unite directly with Me_2S and its homologues, forming hydrobromides of '**thetines**' (Crum Brown a. Letts, *B.* 7, 695).

Salts.—The NH_4, K, Ba, and Ca salts are v. sol. water.—PbA'$_2$: laminæ, sl. sol. cold water.—AgA': crystalline; explodes at 90°.—$Ur_2O_2NaA'_3$ (Clarke a. Owens, *B.* 14, 35).

Methyl ether MeA'. (144°) (P. a. D.).

Ethyl ether EtA'. (159°). Converted by Na into aceconitic ether (*v.* p. 2).

Chloro-ethyl ether $CH_2Cl.CH_2.A'$. (211°). S.G. $\frac{11}{?}$ 1·65. From chloro-ethyl chloro acetate and Br (Henry, *C. R.* 97, 1308). Decomposed by heating with water into glycol chlorhydrin and bromo-acetic acid.

Bromo-ethyl ether
$CH_3.CHBr.O.CO.CH_2Br$. (135°) at 370 mm. S.G. ^{17} 1·962. From $CH_3.CHCl.OAc$ (*v.* p. 105) and Br at 100° (Kessel, *B.* 10, 1999; 11, 1916). Oil. Boiling alcoholic KOH forms bromo-acetic ether, EtBr, acetal, and crotonic aldehyde.

Di-bromo-ethyl ether
$C_2H_3Br_2.O.CO.CH_2Br$. A non-volatile oil, obtained by heating the preceding (1 mol.) with Br (1 mol.) at 120°.

Tri-bromo-ethyl ether
$C_2H_2Br_3.O.CO.CH_2Br$. An oil formed by heating bromo-ethyl bromo-acetate (1 mol.) with Br (2 mols.) at 160°.

Tetra-bromo-ethyl-ether
$C_2HBr_4.O.CO.CH_2Br$. (177°). From the preceding (1 mol.) and Br (1 mol.) at 170°. Decomposed by alcohol into EtBr and bromo- and di-bromo-acetic ethers.

Penta-bromo-ethyl ether
$C_2Br_5.O.CO.CH_2Br$. (c. 197°). Formed by brominating the preceding.

Isoamyl ether $C_5H_{11}A'$. (207°).

Chloride v. BROMO-ACETYL CHLORIDE.

Bromide v. BROMO-ACETYL BROMIDE.

Anhydride $(CH_2Br.CO)_2O$. (245°). Obtained by distilling $Ac.O.CO.CH_2Br$ which is formed by the action of AcONa on $Br.CO.CH_2Br$ (Naumann, *A.* 129, 273; Gal, *C. R.* 71, 273).

Amide $CH_2Br.CO.NH_2$. [165°]. From bromo-acetic ether and 20 p.c. NH_3 at 0° (Kessel, *B.* 11, 2116). V. sol. water, sl. sol. alcohol, insol. ether.

Nitrile $CH_2Br.CN$. (149°). S.G. $\frac{12}{}$ 1·771. V.D. 4·06. Bromo-acetonitrile is formed by the action of bromine-water on iodo-acetonitrile (Henry, *C. R.* 103, 413). The dibromide of acetonitrile (p. 35) may be looked upon as a hydrobromide of bromo-acetonitrile; when water is added to its alcoholic solution needles of the imide $(CH_2Br.CO)_2NH$ [98°] gradually separate (Engler, *A.* 133, 137; 142, 69).

Di-bromo-acetic acid $CHBr_2.CO_2H$. [45°-50°]. (233°). Formed, together with $CH_2Br.CO_2H$, when a mixture of bromine and acetic acid is exposed to sunlight (Perkin a. Duppa, *C. J.* 11, 22; Schäffer, *B.* 4, 368). Formed also by the action of Br on acetic ether at 130° (Carius, *B.* 3, 336), and as a by-product in the preparation of tri-bromo-acetic aldehyde by passing bromine-vapour into alcohol. Crystalline mass, v. sol. alcohol and ether; its vapour is very pungent.

Salts. Excepting Ag and mercurous salts, the dibromo-acetates dissolve readily in water. NH_4A'. KA'aq. $BaA'_2$4aq. $BaA'_2$6aq (Benedikt, *A.* 189, 160).—PbA'_2: stellate groups of needles.—AgA': needles; decomposed by boiling water into AgBr, glyoxylic acid, and dibromo-acetic acid; decomposed by ether at 100° into AgBr and an oil, $C_4H_4Br_2O_4$, whence water forms di-bromo-acetic and glyoxylic acids (Perkin, *C. J.* 32, 91).

Ethyl ether $CHBr_2.CO_2Et$. (193°). Formed by heating the acid with alcohol or by adding bromal-hydrate (4 pts.) to an alcoholic solution of KCy (1 pt.) (Remi, *J. R.* 7, 263).

Amide $CHBr_2.CO.NH_2$. [156°]. *Formation.*—1. From di-bromo-acetic ether and NH_3 (Schäffer, *B.* 4, 369; Kessel, *B.* 11, 2116).—2. From penta-bromo-aceto-acetic amide $CBr_3.CO.CBr_2.CO.NH_2$ and boiling water (Stokes a. V. Pechmann, *Am.* 8, 375).—3. From penta-bromo-acetone and NH_3 (Cloez, *A.* 122, 121).—4. From asparagine and bromine (Guareschi, *B.* 9, 1435). *Properties.*—Needles; may be sublimed; m. sol. cold, v. sol. hot, water, alcohol, and ether.

Nitrile $CHBr_2.CN$. [112°]. Formed, together with bromoform and CO_2 by the action of Br on aqueous cyano acetic acid (Hoff, *B.* 7, 1571).

Tri-bromo-acetic acid $CBr_3.CO_2H$. [130°] (S.); [135°] (Gal, *C. R.* 77, 786). (250°).

Formation.—1. By the action of water on tri-bromo-acetyl bromide.—2. By heating aqueous malonic acid with bromine (Petrieff, *B.* 8, 730).—3. By heating tri-bromo-acetic aldehyde with HNO_3 (Schäffer, *B.* 4, 370).

Properties. Monoclinic tables, v. sol. water; its vapour is pungent. Decomposed by boiling, giving off Br and HBr. The salts, excepting the silver and mercurous salts, are v. sol. water and alcohol, but decomposed by heat, both when dry and when in solution, into bromoform and a metallic carbonate.

Salts.—$NaA'2\frac{1}{2}aq$: lustrous laminæ.—$BaA'_2$3aq: tables.—PbA'_2: stellate groups of needles.—AgA': very unstable laminæ.

Ethyl ether EtA'. (225°).

Amide $CBr_3.CO.NH_2$. [121°]. Formed, together with the preceding by the action of bromine on asparagine suspended in water (Guareschi, *G.* 6, 375). Formed also by treating hexa-bromo-acetone with ammonia (Weidel a. Grüber, *B.* 10, 1148). Monoclinic laminæ; may be sublimed; sl. sol. alcohol, ether, and cold water. Split up by boiling alkalis into bromo-form, CO_2, and NH_3.

BROMO-ACETIC ALDEHYDES.

Bromo-acetic ortho-aldehyde.

Ethyl ether $CH_2Br.CH(OEt)_2$. *Bromo-acetal.* (171°). From acetal and bromine (Pinner, *B.* 5, 119) or by treating vinyl ethyl oxide with Br and decomposing the product $CH_2Br.CHBr.OEt$ with NaOEt (Wislicenus, *A.* 192, 112). Alcoholic KOH at 170° converts it into $CH_2OH.CH(OEt)_2$, while NaOEt forms at 100° $CH_2(OEt).CH(OEt)_2$.

Di-bromo-acetic aldehyde $CHBr_2.CHO$. (142°). Formed by dropping Br (2 mols.) into a solution of paraldehyde (1 mol.) in acetic ether (Hagemann, *B.* 3, 758; Pinner, *A.* 179, 67). Liquid, v. sol. water and alcohol. Blisters the skin. Slowly changes to an isomeric modification, insol. water. Combines with water, forming the solid hydrate $CHBr_2.CH(OH)_2$.

Tri-bromo-acetic aldehyde $CBr_3.CHO$. *Bromal.* Mol. w. 281. (174°). S.G. 3·34.

Formation.—1. By the action of Br on alcohol (Löwig, *A.* 3, 280; Schäffer, *B.* 4, 366).—2. Together with the preceding, by the bromination of paraldehyde.

Properties. Pungent liquid; decomposed by aqueous alkalis into bromoform and formic acid.

Reactions.—1. Fuming HNO_3 forms tri-bromo-acetic acid.—2. Alcoholic KCy forms di-bromo-acetic ether and HCy (Remi, *B.* 8, 695).—3. Conc. H_2SO_4 forms *bromalide* $C_5H_2Br_6O_3$ or tri-bromo-ethylidene tri-bromo-lactate

$$CBr_3.CH\left\langle\begin{array}{l}O.CO\\ \quad|\\ O.CH.CBr_3\end{array}\right.$$

[158°]. This body is also formed by the action of tri-bromo-lactic acid on bromal (Wallach, *A.* 193, 52). It is insol. water, and decomposed by alcohol.—4. *Tri-chloro-lactic acid* forms the corresponding

$$CBr_3.CH\left\langle\begin{array}{l}O.CO\\ \quad|\\ O.CH.CCl_3\end{array}\right.$$

[150°].—5. *Lactic acid* forms

$$CBr_3.CH\left\langle\begin{array}{l}O.CO\\ \quad|\\ O.CH.CH_3\end{array}\right.$$

[97°] (Klimenko, *B.* 9, 968).

Combinations.—1. With water: *Tri-bromo-acetic orthoaldehyde* or *Bromal-hydrate* $CBr_3.CH(OH)_2$. [54°]. Crystallises on evaporating an aqueous solution of bromal. Decomposed by distillation into H_2O and bromal.—2. With alcohol: $CBr_3.CH(OH)(OEt)$. *Bromal alcoholate* [44°]. Thick needles; sl. sol. water; resolved by distillation into its components.—3. With sodium bisulphite $CBr_3.CH(OH).SO_3Na$: laminæ.—4. With ammonia $CBr_3.CH(OH).NH_2$: crystals, insol. water; decomposed at 35° (Schiff a. Tassinari, *B.* 10, 1786).—5. With acetamide: $CBr_3.CH(OH).NHAc$. [160°] (S. a. T.).—6. With

ethyl carbamate: $CBr_3.CH(OH).NH.CO_2Et$. *Bromal-urethane* [132°] (Bischoff, *B.* 7, 632).

BROMO-ACETIC BROMIDE *v.* BROMO-ACETYL BROMIDE.

BROMO-ACETIC CHLORIDE *v.* BROMO-ACETYL CHLORIDE.

BROMO-ACETIC OXIDE *v.* *Anhydride of* BROMO-ACETIC ACID.

BROMO-ACETO-ACETIC ACID *Ethyl-ether* $C_6H_9BrO_3$ *i.e.* $CH_3.CO.CHBr.CO_2Et$. S.G. [23] 1·511.

Formation.—By addition of Br (1 mol.) to an ethereal solution of aceto-acetic ether (Duisberg, *B.* 15, 1378; *A.* 213, 138).

Properties.—Pungent brown liquid; sl. sol. water, v. sol. ether and alcohol. Gradually decomposes on standing, giving off HBr. Fe_2Cl_6 turns its aqueous solution deep red. It is dissolved by baryta-water, and on adding $Cu(OAc)_2$ the solution gives a sap-green crystalline pp. $Cu(C_6H_8BrO_3)_2$ which on recrystallisation from alcohol or CS_2 separates as dark-green needles.

Reactions. 1. Alcoholic NH_3 forms succinyl-succinic ether. 2. Na added to its ethereal solution also produces succinyl-succinic ether (dihydride of di-oxy-terephthalic ether).—3. NaOEt produces succinyl-succinic acid (Wedel, *A.* 219, 92). These reactions may be represented thus: $2CH_3.CO.CHBr.CO_2Et$

$$= 2HBr + \begin{array}{l} CH_2.CO.CH.CO_2Et \\ \quad | \qquad\quad | \\ CO_2Et.CH.CO.CH_2 \end{array}$$

$$= 2HBr + \begin{array}{l} CH:C(OH).CH.CO_2Et \\ \quad | \qquad\qquad | \\ CO_2Et.CH.C(OH):CH \end{array}$$

Anilide $CH_3.CO.CHBr.CO.NHPh$. [138°]. Bromine added to the anilide of aceto-acetic ether in chloroform forms an additive product which on warming yields bromo-aceto-acetic anilide (Knorr, *A.* 236, 79). Pearly plates (from alcohol); sl. sol. water. Conc. H_2SO_4 produces bromo-oxy-methyl-quinoline.

Methyl-bromo-aceto-acetic ether

$CH_3.CO.CMeBr.CO_2Et$. Obtained by bromination of methyl-aceto-acetic ether. Liquid. Converted by heat into EtBr and $C_6H_8O_3$ (Pawlow, *C. R.* 97, 99).

Ethyl-bromo-aceto-acetic ether

$CH_3.CO.CEtBr.CO_2Et$. S.G. 1·35. Obtained by adding Br to ethyl-aceto-acetic ether in ethereal solution (Wedel, *A.* 219, 102). Pungent liquid. Fe_2Cl_6 turns its alcoholic solution violet. At 100° it gives EtBr and $C_{14}H_{16}O_6$ or $C_7H_8O_3$, probably $CH_3.CO.C(CO_2H):CH.CH_3$ (*cf.* Demarçay, *A. Ch.* [5] 20, 465).

Iso-butyl-bromo-aceto-acetic ether

$CH_3.CO.C(C_4H_9)Br.CO_2Et$. From iso-butyl-aceto-acetic ether and Br at −5° (Demarçay, *Bl.* [2] 31, 513; 33, 516; *A. Ch.* [5] 20, 433; *C. R.* 86, 1085, 1135). Alcoholic KOH converts it, according to Demarçay, into hexoic, methyl-isobutyl-glyceric, heptoic, oxyheptoic, and glycollic acids; according to Pawlow (*C. R.* 97, 99) alcoholic KOH forms an acid $C_8H_{12}O_3$ or $CH_3.CO.C(CO_2H):CH.Pr$ with evolution of EtBr.

Di-bromo-aceto-acetic ether

$CH_3.CO.CBr_2.CO_2Et(?)$. S.G. [23] 1·884. From aceto-acetic ether (10 g.) in ether (10 g.) treated with Br (24·6 g.) (Duisberg, *A.* 213, 143). Pungent oil.

Reactions.—1. Aqueous Fe_2Cl_6 gives a deep red colour.—2. *Baryta-water* gives a claret colour, but $Cu(OAc)_2$ gives no pp. in this solution. A sap-green pp. $Cu(C_6H_7Br_2O_3)_2$ is, however, formed when conc. $Cu(OAc)_2Aq$ is added to an alcoholic solution of the ether; it crystallises in needles (from alcohol).—3. Diluted with ether and treated with Na, di-bromo-aceto-acetic ether (80 g.) gives di-oxy-terephthalic ether (2 g.). NaOEt may be used instead of Na (Wedel, *A.* 219, 74).

Ethyl-di-bromo-aceto-acetic ether

$C_6H_7Br_2EtO_3$ *i.e.* $CH_2Br.CO.CBrEt.CO_2Et$ (?). S.G. 1·61. A yellowish oil, got by bromination of ethyl-aceto-acetic ether. Fe_2Cl_6 colours its alcoholic solution wine red (Wedel, *A.* 219, 102).

Tri-bromo-aceto-acetic ether

$CH_2Br.CO.CBr_2.CO_2Et$. S.G. [22] 2·114. From aceto-acetic ether (10 g.) in chloroform (20 g.) by addition of bromine (38 g.) (Duisberg, *A.* 213, 145). Yellow liquid, slightly pungent. V. sl. sol. water. When heated, it gives off HBr.

Reactions.—1. Aqueous Fe_2Cl_6 gives after some time a slight red pp.—2. Gives in alcoholic solution with cupric acetate a green pp. $Cu(C_6H_6Br_3O_3)_2$ (Wedel, *A.* 219, 95).

Ethyl-tri-bromo-aceto-acetic ether

$C_6H_5Br_3EtO_3$ *i.e.* $CHBr_2.CO.CBrEt.CO_2Et$ (?). S.G. 1·86. Its alcoholic solution is turned wine-red by Fe_2Cl_6.

Tetra- and Penta-bromo-aceto-acetic ethers, so called, are mixtures of tri- with per- bromo-aceto-acetic ether.

Penta-bromo-aceto-acetamide

$CBr_3.CO.CBr_2.CO.NH_2$. [c. 148°]. From di-oxy-amido-pyridine and bromine water (Stokes a. V. Pechmann, *Am.* 8, 375). Needles or prisms; converted by boiling water into di-bromo-acetamide and $CHBr_3$. Alcoholic NH_3 gives di-bromo-malonamide and $CHBr_3$.

Per-bromo-aceto-acetic ether $C_6Br_{10}O_3$ *i.e.* $CBr_3.CO.CBr_2.CO_2C_2Br_5$. [69°-70°]. From tri-bromo-aceto-acetic ether and bromine at 80° for 2 days. Colourless crystalline mass. Not affected by air. Gives no colour with Fe_2Cl_6 and no copper pp. (Wedel, *A.* 219, 97).

BROMO-ACETO-AMIDO- *v.* BROMO-AMIDO-.

TRI-BROMO-ACETO-GUANAMIDINE

$C_4H_4Br_3N_5O_3$. From bromine and aqueous acetoguanamide (Nencki, *B.* 9, 236). Minute needles, insol. water, alcohol, and ether. Split up by boiling with water into bromoform and cyanuric acid.

BROMO-ACETOL *v.* DI-BROMO-PROPANE.

BROMO-ACETONE $CH_3.CO.CH_2Br$. S.G. 1·99.

Formation.—1. By adding 1 mol. bromine to acetone, either pure or mixed with water or with CS_2 (Linnemann, *A.* 125, 307; Emmerling, *B.* 6, 22). 2. By the action of a weak electric current on a mixture of acetone and HBr (Riche, *C. R.* 49, 276).

Preparation.—1. A stream of dry air saturated with bromine (138 g.) is passed through 100 g. cooled acetone (Emmerling a. Wagner, *A.* 204, 27).—2. Bromine (1 mol.) is passed through a solution of 1 mol. acetone in 10 vol. water (Sokolowsky, *B.* 9, 1687).

Properties.—Yellow, very pungent-smelling oil, quickly turning violet when dry, more permanent when mixed with a little water. Ag_2O oxidises it to formic and acetic acids (Linnemann, *Sitz. B.* 68, 137). Aqueous K_2CO_3 forms

a syrupy acid $C_{12}H_{18}O_7$ (?) Bromo-acetone combines with $NaHSO_3$.

u-Di-bromo-acetone $CH_3.CO.CHBr_2$. S.G. 2·5. Prepared by adding bromine (2 mols.) to acetone (1 mol.) mixed with a large quantity of water. Liquid, volatile with steam. Not very pungent. Combines with $NaHSO_3$.

s-Di-bromo-acetone $CH_2Br.CO.CH_2Br$. [24°]. From di-iodo-acetone and AgBr at 150°; or from di-chloro-acetone and aqueous KBr. Long needles with pungent smell (Völker, *A.* 192, 96). Reduced by Zn and H_2SO_4 to acetone.

Tri-bromo-acetone $CBr_3.CO.CH_3$. Formed by the action of alkalis upon hexa-bromo-methyl methenyl di-ketone. NH_3 gives bromoform (Combes, *A. Ch.* [6] 12, 241).

Tetra-bromo-acetone hydrate $C_3H_2Br_4O$ 2aq. [43°]. From Br (10 pts.) and acetone (1 pt.) in the cold; when the resulting solid mass is recrystallised from dilute alcohol a mixture of tetra- and penta-bromo-acetone is first deposited, and afterwards prisms of tetra-bromo-acetone hydrate $C_3H_2Br_4O$ 2aq. The hydrate is insol. water, sol. alcohol (Mulder, *J.* 1864, 330). Perhaps this body is $(C_3H_2Br_4O)HOEt$.

Penta-bromo-acetone C_3HBr_5O. [76°].

Formation.—1. From Br (12 pts.) and acetone (1 pt.) (Mulder, *J.* 1864, 330; *cf.* Steiner, *B.* 7, 505, 1281). 2. Separates on adding water to an alcoholic solution of 'phlorobromin,' that has stood some time (Benedikt, *C. C.* 1878, 101; *A.* 189, 168).—3. From potassic citraconate and Br (Cahours, *A.* 64, 351; Grimaux, *J.* 1874, 522).—4. From chelidonic acid and Br (Wilde, *A.* 127, 167).—5. From aqueous pyruvic acid and Br at 100° (Wichelhaus, *A.* 152, 260).

Properties.—Trimetric needles (from dilute alcohol); $a:b:c = \cdot698 : 1 : \cdot686$ (Ditscheiner a. Friedländer, *Z. Kryst.* 3, 103). Converted by aqueous or alcoholic NH_3 into di-bromo-acetamide. Aqueous KOH forms bromoform, HBr, CO_2, and formic acid.

Hexa-bromo acetone $CBr_3.CO.CBr_3$. [112°].

Formation.—1. By the action of Br on an aqueous solution of tri-amido-phenol hydrochloride or hydrobromide, or on 'bromo-dichromazin' the first product of the action of bromine on these salts. 2. From bromanilic acid and Br (Hantzsch a. Schniter, *B.* 20, 2040). 3. From di-amido-guaiacol hydrochloride and Br (Herzig, *M.* 3, 825).

Properties.—Monoclinic prisms (from chloroform), insol. water. Decomposed by alcohol.

Reactions. 1. Boiling NaOHAq or water at 180° form bromoform and CO_2.—2. Boiling conc. HNO_3 has no action, but at 150° it produces bromo-picrin CBr_3NO_2.—3. Dry NH_3 gives rise to tri-bromo-acetamide and CBr_3H.—4. *Sodium amalgam* reduces it to iso-propyl alcohol.

BROMO-ACETONITRILE *v.* Nitrile of Bromo-acetic acid.

ω-BROMO-ACETOPHENONE C_8H_7BrO *i.e.* $C_6H_5.CO.CH_2Br$. *Phenyl bromo-methyl ketone. Phenacyl bromide.* [50°].

Formation.—1. From acetophenone and Br (Emmerling a. Engler, *B.* 4, 148; Hunnius, *B.* 10, 2006; Staedel, *B.* 13, 837).—2. Formed, together with CO_2 and HBr, by boiling α-phenyl-α-oxy-β-dibromo-propionic acid with water (Böttinger, *B.* 14, 1238).

Preparation.—133½ pts. of bromine are slowly run into a mixture of 100 pts. of acetophenone and 500 pts. of glacial acetic acid. After standing an hour it is gently heated on a water bath till colourless, when it is at once poured into a large quantity of cold water; the yield is 133 pts. or 80 p.c. of the theoretical (Möhlau, *B.* 15, 2464).

Properties.—Trimetric prisms (from dilute alcohol); pungent; v. sol. alcohol and ether, insol. water.

Reactions.—1. $KMnO_4$ forms benzoic acid.—2 Alcoholic NH_3 forms iso-indole C_8H_7N.—3. With *sodio-malonic ether* it forms $C_6H_5.CO.CH_2.CH(CO_2H)_2$.—4. With *sodio-aceto-acetic ether* it forms acetophenone-aceto-acetic ether (*v.* p. 36).—5. *Aniline* forms phenyl-amido-acetophenone (Möhlau, *B.* 14, 172).—6. Reacts with *hydroxylamine hydrochloride* with production of iso-nitroso-acetophenone-oxim, $C_6H_5.C(NOH).CH_2.NH.OH$ [163°] (Schramm, *B.* 16, 2183).—7. An alcoholic solution of phenyl hydrazine reacts thus: $Ph.CO.CH_2Br + N_2H_3Ph = HBr + H_2O + Ph.C_2H_2N_2Ph$. The product forms yellow needles (from alcohol) [137°]. It is very soluble in ether, chloroform, and CS_2, less in alcohol or light petroleum. It is decomposed by acids (O. Hess, *A.* 232, 234).

ω-Di-bromo-acetophenone $C_6H_5.CO.CHBr_2$. [37°]. Prepared by adding bromine (2 mols.) to a cold solution of acetophenone (1 mol.) in acetic acid, warming to 65°–70°, and pouring into water; the yield is c. 80 p.c. of the theoretical (Engler a. Hassenkamp, *B.* 18, 2240; *cf.* Hunnius, *B.* 10, 2010; Fittig a. Wurster, *A.* 195, 161).

Properties.—Trimetric tables (from CS_2); insol. water. Oxidised by $KMnO_4$ to benzoic acid.

Reactions.—1. Alcoholic KOAc forms $Ph.CO.CH(OAc)_2$.—2. Alcoholic *hydroxylamine* forms phenyl-glyoxim Ph.C(NOH).CH(NOH) [152°].—3. By treatment with NH_3 a portion breaks up into benzamide and CH_2Br_2 whilst another part yields isoindileucine $C_{16}H_{12}N_2O$.

ω-TRI-BROMO-ACETOPHENONE-o-CARBOXYLIC ACID $CBr_3.CO.C_6H_4.CO_2H$. [160°]. From phthalyl-acetic acid and Br. Resolved by alkalis into $CHBr_3$ and phthalic acid (Gabriel a. Michael, *B.* 10, 1551, 2199; 11, 1007).

BROMO-ACETOTHIENONE *v.* Thienyl bromo-methyl ketone and Bromo-thienyl methyl ketone.

HEXA-BROMO-ACETYL-ACETONE *v.* Hexa-bromo-di-methyl-methylene di-ketone.

BROMO-ACETYL-BENZENE is Bromo-acetophenone (*q.v.*).

BROMO-ACETYL BROMIDE $CH_2Br.CO.Br$. (150°). S.G. ^{21} 2·317.

Formation.—1. From AcBr and Br at 100° (Gal, *A.* 129, 54).—2. From AcBr and PBr_5 at 150° (Samosadsky, *Z.* [2] 6, 105).—3. From AcCl (64 pts.) and Br (120 pts.) at 100° (Hübner, *A.* 124, 315; Naumann, *A.* 129, 257; Gal, *A.* 132, 179).—4. By direct combination of *u*-di-bromo ethylene $CBr_2:CH_2$ with oxygen (Demole, *C. R.* 86, 542).

Properties.—Pungent liquid: blisters the skin.

Reactions.—1. Aqueous Na_2CO_3 forms sodium bromo-acetate and sodium glycollate.—2. Distillation with NaOAc produces Ac_2O, bromo-acetic anhydride and glycollide.—3. $ZnMe_2$ gives a compound whence water liberates

methyl-isopropyl-carbinol, acetone, and methyl ethyl ketone (Winogradow, *A.* 191, 127).

Di-bromo-acetyl bromide $CHBr_2.CO.Br$. (194°). From the preceding and Br at 150° (G.). Formed also by the action of oxygen on tri-bromo-ethylene (D.). Fuming liquid; converted by alcohol into di-bromo-acetic ether.

Tri-bromo-acetyl bromide $CBr_3.CO.Br$. (220°-225°). From the preceding and Br at 200° (G.). Slowly converted by water into tri-bromo-acetic acid.

BROMO-ACETYL CHLORIDE $CH_2Br.COCl$. S.G. ⁹ 1·91. Pungent liquid, produced by the action of PCl_3 on bromo-acetic acid (Wilde, *A.* 132, 171).

BROMO-ACETYL CYANIDE $CH_2Br.CO.CN$. [79°]. Formed, together with $CH_2CN.CO.Br$ by the action of AgCy on bromo-acetyl bromide (Hübner, *A.* 131, 68). Monoclinic tables, decomposed by water into HCy and $CH_2Br.CO_2H$.

BROMO-ACETYLENE CBr:CH. Formed by the action of alcoholic KOH on $CH_2Br.CBr_3$ (Reboul, *A.* 125, 81), on $CH_2Br.CHBr_2$ (Alexejeff, *Z.* 6, 641), or on CHBr:CHBr (Sawitsch, *A.* 119, 183; Fontaine, *C. R.* 70, 1361; Sabanéeff, *Bl.* [2] 45, 245).

Preparation.—Acetylene dibromide is heated with NaOH and dilute alcohol in an apparatus filled with nitrogen. The gas is condensed by a freezing-mixture (S.).

Properties.—Gas at ordinary temperatures; m. sol. water. In the liquid form it is decomposed by light into s-tri-bromo-benzene and other products. It takes fire in air; when slowly mixed with air bromo-acetic acid is formed. Ammoniacal cuprous chloride gives a red pp. of cuprous acetylide. Br forms $CHBr_2.CBr_3$.

β-BROMO β-ACETYL-PROPIONIC ACID $C_5H_7BrO_3$ *i.e.* $CH_3.CO.CHBr.CH_2.CO_2H$. *Bromo-levulic acid.* [59°]. Crystallised from CS_2.

Formation. 1. By bromination of a solution of β-acetyl-propionic acid in conc. HCl below 0°. 2. By the action of water upon (α)-angelico-lactone dibromide (Wolff, *A.* 229, 266; *v.* DI-BROMO-OXY-VALERIC ACID).

Properties. White needles (from CS_2). Sol. alcohol, ether, and water.

Reactions.—By the action of aqueous Na_2CO_3 it yields oxy-acetyl-propionic acid and acet-acrylic acid. By heating with conc. aqueous NH_3 at 110°-120° di-methyl ketine (tetra-methyl-pyrazine) $C_4Me_4N_2$ is formed, with evolution of CO_2. With aniline it gives di-phenyl-tetra-methyl-di-hydro pyrazine $C_4Me_4N_2Ph_2$ (Wolff, *B.* 20, 425).

Ethyl ether EtA′. (240°). S.G. ¹⁵ 1·439. From Br and ethyl β-acetyl-propionate (Conrad a. Guthzeit, *B.* 17, 2285). Malonic ether and NaOEt convert it into methyl propyl ketone tri-carboxylic ether $(CO_2Et)_2CH.CHAc.CH_2.CO_2Et$ (c. 283°) S.G. ¹² 1·097.

Di-bromo-β-acetyl-propionic acid $C_5H_6Br_2O_3$. [115°]. Solidifies about 91°. From β-acetyl-propionic acid, chloroform and Br. From bromo-β-acetyl-propionic acid and bromine. Long thin needles (Wolff, *A.* 229, 266; Hell a. Kehrer, *B.* 17, 1981).

Tri-bromo-β-acetyl-propionic acid $C_5H_5Br_3O_3$. [82°]. From β-acetyl-propionic acid, Br and chloroform (Wolff, *A.* 229, 267).

BROMO-*pseudo*-ACETYL-PYRROL *v.* BROMO-PYRRYL-METHYL KETONE.

BROMO-ACETYL-UREA *v.* UREA.

BROMO- ACIDS *v.* BROMO- COMPOUNDS.

BROMO-MET-ACROLEIN $(C_3H_3BrO)_3$(?). [78°]. Acrolein takes up Br forming di-bromo-propionic aldehyde, a liquid which polymerises, becoming a gummy mass, which may also be obtained by the action of Br on metacrolein. NaOEt converts this gummy metacrolein dibromide into bromo-met-acrolein (Grimaux a. Adam, *Bl.* [2] 36, 136). Needles (from alcohol). Has no smell; does not reduce Fehling's solution. When distilled with H_2SO_4 (1 vol.) diluted with water (1 vol.) it gives off extremely pungent vapours which may be condensed to a liquid, sol. water, which is probably bromo-acrolein. By heating with NaOEt it is converted into $C_6H_7BrO_4$ [140°].

α-BROMO-ACRYLIC ACID $C_3H_3BrO_2$ *i.e.* $CH_2:CBr.CO_2H$. [70°]. From αα or αβ-di-bromo-propionic acid and alcoholic KOH (Philippi a. Tollens, *A.* 171, 333; Wagner a. Tollens, *A.* 171, 340; Erlenmeyer, *B.* 14, 1867).

Properties.—Rectangular monoclinic plates, v. sol. water and alcohol. Decomposed by distillation or exposure to light. Combines with HBr forming αβ-di-bromo-propionic acid.

Salts.—AgA′. BaA′₂ 4aq. CaA′₂ 4aq.—KA′. NaA′aq. NH_4A'. ZnA'_2.

Ethyl ether EtA′. (c. 157°). (77°) at 30 mm. With sodium malonic ether it gives $CO_2Et.C(CH_2).CH(CO_2Et)_2$ identical with the compound from αβ-di-bromo-propionic ether and di-sodium-malonic ether (Michael, *J. pr.* [2] 35, 134).

β-Bromo-acrylic acid $CHBr.CH.CO_2H$. [116°]. From bromalide or from tri-chloro-ethylidene tri-bromo-lactate by reduction with Zn and HCl (Wallach, *A.* 193, 55). Formed also by the addition of HBr to propiolic acid (Bandrowski, *B.* 15, 2702; Stolz, *B.* 19, 540). Plates or needles, sol. water and chloroform; explodes on heating.

Acryl colloids. This name is applied by Wagner a. Tollens to three bodies having the composition $(C_3H_4O_2)x$.

α-*Acryl-colloid.* Is formed in the preparation of α-bromo-acrylic acid from αβ-di-bromo-propionic acid, especially when the action becomes violent. Insol. water, alcohol, and ether, sol. NH_3Aq and not reppd. by HCl.

β-*Acryl-colloid* is formed when α-bromo-acrylic acid is left over H_2SO_4. It is a porous mass, sol. NH_3Aq and reppd. by HCl.

γ-*Acryl-colloid* is formed with separation of EtBr, by heating ethyl α-bromo-acrylate. Amorphous; insol. NH_3Aq, but becoming gummy therein.

αβ Di-bromo-acrylic acid $CHBr:CBr.CO_2H$. [85°]. S. 5·19 at 18°.

Formation. 1. From mucobromic acid and cold baryta-water (Jackson a. Hill, *B.* 11, 1673; *Am.* 3, 111; 4, 169, 273; Hill a. Andrews, *P. Am. A.* 16, 192; 17, 133). 2. From alcoholic KOH and ααβ-tri-bromo-propionic acid (Michael a. Norton, *Am.* 2, 18; Mauthner a. Suida, *Sitz. B.* 83, 273; *M.* 1, 104). 3. From αββ tri-bromo-propionic acid and alcoholic KOH.

Properties. Pearly plates (from alcohol). Sol. ether and chloroform, sl. sol. benzene and CS_2. Boiling baryta-water forms bromo acetylene,

CO_2, formic, malonic, and bromo-propiolic acids. Heated with Br in a sealed tube it forms tetra-bromo-propionic acid.

Salts.—AgA': slender needles.—PbA'_2 aq: pearly plates, sl. sol. cold water.—BaA'_2 aq. S. 6·28 at 18°.—CaA'_2 3aq: long needles.—KA'.

ββ-Di-bromo-acrylic acid CBr_2:CH.CO_2H. [86°]. S. 3·06 at 20°. From tri-bromo-succinic acid by heating with water (Fittig a. Petri, *A.* 195, 70). Formed also by the union of HBr with bromo-propiolic acid (Hill, *B.* 12, 660; Hill a. Mabery, *P. Am. A.* 16, 211).

Properties. Large plates; boils with partial decomposition at 243°-250°. V. e. sol. alcohol, and ether; m. sol. cold water. Does not combine with HBr in the cold. Does not combine with Br in the cold, but at 100° it forms tetra-bromo-propionic acid (Mabery a. Robinson, *Am.* 5, 251).

Salts.—BaA'_2 2aq: S. 12·64.—CaA'_2 $3\frac{1}{2}$aq.

Ethyl ether EtA'. (213°).

Tri-bromo-acrylic acid CBr_2:CBr.CO_2H. [118°]. S. 1·37 at 20°. From αββß-tetra-bromo-propionic acid and alcoholic KOH at 60° (Mauthner a. Suida, *M.* 2, 109). Formed also by treating bromo-propiolic acid with bromine-water (Hill, *Am.* 3, 178); and from di-bromo-iodo-acrylic acid and Br at 100° (Mabery a. Lloyd, *Am.* 4, 92). Monoclinic prisms, $a:b:c$ = ·502:1:·559 (Melville, *P. Am. A.* 17, 151). Triclinic pyramids, $a:b:c$ = 1·128:1:1·150; α = 89° 13′, β = 62° 26′, γ = 91° 14′ (Becke, *M.* 2, 111). V. sol. alcohol and ether. Does not combine with bromine, even at 200°. The Ba salt yields tri-bromo-ethylene when boiled with water.

Salts.—BaA'_2 5aq. BaA'_2 3aq. S. (of BaA'_2) 80·6.—CaA'_2 3aq. AgA'.

BROMO-ADIPIC ACID $C_6H_9BrO_4$. From adipic acid and Br (1 mol.) at 160° (Gal a. Gay-Lussac, *C. R.* 70, 1175). Dark-brown mass, smelling like camphor; converted by boiling alkalis into adipomalic (or oxyadipic?) acid (*v.* p. 64).

(α)-di-bromo-adipic acid $C_6H_8Br_2O_4$. From adipic acid Br (2 mols.) at 160° (G. a. G.). Powder; decomposed by water. Water at 150° forms adipotartaric (or di-oxy-adipic ?) acid (*v.* p. 64).

(β)-di-bromo-adipic acid $C_6H_8Br_2O_4$ [115°-122°]. Formed together with bromo-hydromuconic acid, by the action of Br on a solution of hydromuconic acid (Limpricht, *A.* 165, 265). Needles. Converted by moist Ag_2O or baryta into di-oxy-adipic acid.

(γ)-di-bromo-adipic acid $C_6H_8Br_2O_4$ [175°-190°]. Formed by adding Br to a warm solution of hydromuconic acid in glacial HOAc (L.) Small needles. Converted by moist Ag_2O into muconic acid, and by sodium-amalgam to hydromuconic acid.

Tri-bromo-adipic acid $C_6H_7Br_3O_4$ [177°-180°]. Formed by treating a hot solution of hydromuconic acid with excess of Br (L.). Small needles. Converted by boiling baryta-water into tri-oxy-adipic acid.

Tetra-bromo-adipic acid $C_6H_6Br_4O_4$. [211°]. Formed by heating hydromuconic acid with Br and water at 100°. Crystalline. V. sl. sol. water, v. sol. alcohol. H. W.

BROMO-ÆSCULETIN *v.* ÆSCULETIN, p. 65.

BROMO-ALDEHYDE *v.* BROMO-ACETIC ALDEHYDE.

BROMO-ALIZARIN *v.* BROMO-DI-OXY-ANTHRAQUINONE.

DI-BROMO-DIALLYL *v.* *Di*-BROMO-HEXINENE.

BROMO-ALLYL ACETATE C_3H_4BrOAc *i.e.* CHBr:CH.CH_2.O.Ac (?). (164°). S.G. 12 1·57. From bromo-allyl bromide (β-epidibromhydrin) and alcoholic KOAc (Henry, *B.* 5, 453). Fragrant liquid; not attacked by PCl_5. H. W.

α-BROMO-ALLYL ALCOHOL C_3H_5BrO *i.e.* CH_2:CBr.CH_2OH. (152°). From α-bromo-allyl bromide (α-epidibromhydrin) and water at 130° (Henry, *B.* 14, 403). Liquid; converted by aqueous KOH into propargyl alcohol.

β-Bromo-allyl alcohol CHBr:CH.CH_2OH(?). (155°). S.G. 15 1·6. From β-bromo-allyl acetate (*v. sup.*) by distillation with solid NaOH (Henry, *B.* 5, 453). Is perhaps identical with the preceding.

DI-BROMO-DI-ALLYL-AMINE $C_6H_9Br_2N$ *i.e.* $(C_3H_4Br)_2$NH. From *s*-tri-bromo-propane (tribromhydrin) and alcoholic NH_3 at 100 (Maxwell Simpson, *P. M.* [4] 16, 257). Also from bromo-allyl bromide and alcoholic NH_3 (Reboul, *A. Suppl.* 1, 232). Alkaline liquid, v. sl. sol. water. Converted by alcoholic NH_3 at 250° into methyl-pyridine.—$B'_2H_2PtCl_6$.—$B'HgCl_2$.

BROMO-ALLYL BROMIDE *v.* DI-BROMO-PROPYLENE.

BROMO-ALLYLENE *v.* PROPARGYL BROMIDE.

Bromo-diallylene *v.* HEXONYL BROMIDE.

BROMO-ALLYL ETHYL OXIDE *v.* ETHYL BROMO-ALLYL OXIDE.

BROMO-ALLYL NITRATE

CHBr:CH.CH_2.O.NO_2 (?). (140°-150°). S.G. 12 1·5. From β-bromo-allyl bromide and $AgNO_3$ (Henry, *B.* 5, 452).

BROMO-ALLYL OXIDE $C_6H_8Br_2O$ *i.e.* $(CHBr:CH.CH_2)_2O$ (?). *Bromo-allyl ether.* (c. 214°). S.G. 17 1·7. Formed together with propargyl alcohol from β-bromo-allyl alcohol and solid KOH (Henry, *B.* 6, 729).

BROMO-ALLYL THIO-CARBIMIDE C_3H_4BrN.CS. (c. 200°). From bromo-allyl bromide and alcoholic potassium sulpho-cyanide (Henry, *B.* 5, 188).

BROMO-ALLYL-THIO-UREA (C_3H_4Br)NH.CS.NH_2. [111°]. From the preceding and ammonia (H.).

TRI-BROMO-ALOÏN *v.* ALOÏN, p. 141.

BROMO-AMIDO-ACETOPHENONE [5:2:1] $C_6H_3Br(NH_2)$.CO.CH_3.

Acetyl derivative

C_6H_3Br(NHAc).CO.CH_3. [160°]. Obtained by bromination of acetyl-*o*-amido-acetophenone in acetic acid solution (Baeyer a. Bloem, *B.* 17, 965). Slender felted colourless needles, sol. hot, sl. sol. cold, alcohol; v. sl. sol. cold water. By $KMnO_4$ it is oxidised to bromo-isatin [255°]. By boiling with KOH it yields bromo-indigo.

ωω-Tri-bromo-*o*-amido-acetophenone [5:2:1] $C_6H_3Br(NH_2)$.CO.$CHBr_2$. [c. 145°]. Fine felted orange yellow needles. V. sol. alcohol and ether, sl. sol water. Obtained by saponification of the acetyl derivative by boiling it with a mixture of alcohol and aqueous HBr.

Acetyl derivative

C_6H_3Br(NHAc).CO.$CHBr_2$: [185°], yellowish granular crystals, v. sol. chloroform, sl. sol.

alcohol. Formed by the action of bromine vapour on dry acetyl-o-amido-acetophenone mixed with a little iodine. By boiling with HCl it yields ω-di-chloro-m-bromo-o-amido-acetophenone. By $KMnO_4$ it is oxidised to bromo-isatin. By boiling with dilute NaOH and exposure to the air it gives bromo-indigo (Baeyer a. Bloem, *B.* **17**, 966).

DI-BROMO-AMIDO-ANTHRAQUINONE $C_{14}H_5Br_2(NH_2)O_2$. [170° uncorr.]. Prepared by reduction of dibromo-nitro-anthraquinone with stannous chloride (Claus a. Dierufeller, *B.* **14**, 1334). Slender red needles. Sl. sol. all solvents. Has no basic properties.

BROMO-AMIDO-BENZENE *v.* BROMO-ANILINE.

(1, 2, 4)-BROMO-AMIDO-BENZENE SULPHONIC ACID $C_6H_6BrNSO_3$ *i.e.* $C_6H_3Br(NH_2)SO_3H$ [1:2:4]. *Bromo-aniline sulphonic acid.* S. 1·49 at 11° (S.); 2·61 at 20° (A.); 1·31 at 4° (La.).

Formation.—1. By reduction of (1, 2, 4)-bromo-nitro-benzene sulphonic acid (Goslich, *A.* 180, 100).—2. By sulphonation of o-bromo-aniline (Andrews, *B.* 13, 2126). 3. From bromo-benzene p-sulphonic acid by nitration and reduction. 4. From very dilute aqueous amido-benzene m-sulphonic acid and bromine-water (Langfurth, *A.* 191, 176). 5. From (1, 3, 4, 6) di-bromo-m-amido-benzene sulphonic acid, fuming HCl, and red P at 150° (Limpricht, *B.* 10, 1542). 6. By heating the same acid with water at 250° (L.).

Properties.—Anhydrous needles (from conc. aqueous solution) or four- and six-sided columns containing aq (from dilute solution). Sl. sol. alcohol. Reduced by HI and P, or by water at 120°, to amido-benzene m-sulphonic acid.

Salts.—KA'1½aq (La.).—KA'aq (Spiegelberg, *A.* 197, 257).—BaA'$_2$aq.—BaA'$_2$3aq. S. (of BaA'$_2$) 6·22 at 17°.—PbA'$_2$.—CaA'$_2$2aq.—AgA'1½aq.

(1, 4, 3)-Bromo-amido-benzene sulphonic acid $C_6H_3Br(NH_2)SO_3H$ [1:4:3]. S. ·47 at 15°.

Formation.—1. By heating p-bromo-aniline ethyl-sulphate (Nölting, *B.* 8, 1095).—2. By adding bromine to a cold aqueous solution of barium aniline o-sulphonate (Limpricht, *A.* 181, 196).—3. By nitration and reduction of bromo-benzene m-sulphonic acid (Thomas, *A.* 186, 126). 4. From acetyl-p-bromo-aniline and fuming H_2SO_4 (Borns, *A.* 187, 368).

Properties.—Slender silky needles (containing aq) or large efflorescent prisms (with 2 aq). Sl. sol. cold water, v. sl. sol. alcohol. Converted by Br into tri-bromo-aniline. HI and P form aniline o-sulphonic acid.

Salts.—NH_4A'.—KA'.—BaA'$_2$aq.—CaA'$_2$aq.—PbA'$_2$2aq.

(1,4,2)-Bromo-amido-benzene sulphonic acid $C_6H_3Br(NH_2)SO_3H$ [1:4:2]. S. 1·14 at 18°. From bromo-benzene o-sulphonic acid by nitration and reduction (Bahlmann, *A.* 181, 203; 186, 318). Needles (from conc. aqueous solutions) or rhombohedra (?) containing 2aq (from dilute aqueous solution); v. sol. hot water, insol. alcohol and ether. Reduced by HI and P to aniline m-sulphonic acid. Salts.—BaA'$_2$2aq: needles, v. e. sol. water.—PbA'$_2$.—AgA'.

Bromo-amido-benzene sulphonic acid $C_6H_3Br(NH_2)(SO_3H)$ [1:x:2]. S. ·74 at 8°. Formed in smaller quantity in the preparation of the preceding (B.). Prisms; sl. sol. cold water.—BaA'$_2$xaq: laminæ, v. sol. water.

Bromo-amido-benzene sulphonic acid $C_6H_3Br(NH_2)(SO_3H)$ [1:3:x]. From acetyl m-bromo-aniline and fuming H_2SO_4 (Borns, *B.* 8, 1072). Needles.—BaA'$_2$2aq.

(1,2,3,5)-Bromo-amido-benzene disulphonic acid $C_6H_2Br(NH_2)(SO_3H)_2$ [1:2:3:5]. Formed by bromination of (1,2,4)-amido-benzene disulphonic acid (Zander, *A.* 198, 1). Needles (containing aq); v. sol. water, sl. sol. alcohol.

Salts.—The acid salts are less soluble than the normal ones.—$(NH_4)_2A''$2aq. BaA''3aq.—$BaH_2A''_2$5aq.—$PbH_2A''_2$5aq. K_2A''2aq.

Bromo-amido-benzene disulphonic acid $C_6H_2Br(NH_2)(SO_3H)_2$ [1:4:3:5] or [4:1:3:5] or [2:1:3:5]. Formed by adding bromine to an aqueous solution of (1 or 4, 3, 5) amido benzene disulphonic acid (Heinzelmann, *A.* 188, 179). Prisms (containing 2½aq); v. e. sol. water.—BaA''3aq. PbA''3aq.

Bromo-di-amido-benzene sulphonic acid $C_6H_2Br(NH_2)_2SO_3H$ [1:2:6:4]. *Bromo-m-phenylene-diamine sulphonic acid.* S. ·51 at 17°. Got by reducing $C_6Br_2(NO_2)_2SO_3H$ with $SnCl_2$ (Bassmann, *A.* 191, 244). Long white needles (containing aq), turns yellow in air. When pure it is sl. sol. water, when impure it is very soluble. Insol. alcohol. Paper moistened with its solution turns red in air. The aqueous solutions of its salts turn blue or red when evaporated. Converted by diazo- reaction into p-bromo benzene sulphonic acid.—BaA'$_2$aq.

(1,3,2,5) Di-bromo-amido-benzene sulphonic acid $C_6H_2Br_2(NH_2)(SO_3H)$ [1:3:2:5]. Formed by adding bromine to an aqueous solution of aniline p-sulphonic acid (Schmitt, *A.* 120, 138; Lenz, *B.* 8, 1066; *A.* 181, 24). Formed also by brominating (1,2,4)-amido-benzene disulphonic acid (Zander, *A.* 198, 16). Needles or prisms (containing 2aq); v. sol. water and hot alcohol; ppd. by conc. H_2SO_4 from its aqueous solution. Br forms tri-bromo aniline.—BaA'$_2$2aq.—BaA'$_2$3½aq. S. (of BaA'$_2$) ·16 at 11°.—PbA'$_2$2aq.—AgA'.

Reactions. PCl_5 forms a product (probably $C_6H_2Br_2(NH.POCl_2)SO_2Cl$) from which alcohol produces $C_6H_2Br_2(SO_2Cl)NH.PO(OEt)_2$. [170°] (Laar, *J. pr.* 128, 256). *V.* also DI-METHYL-AMIDO-BENZENE SULPHONIC ACID.

(1,3,4,6)-Di-bromo-amido-benzene sulphonic acid $C_6H_2Br_2(NH_2)SO_3H$ [1:3:4:6]. S. ·252 at 10°; ·249 at 7°; ·194 at 4° (Berndsen, *A.* 177, 84; Beckurts, *A.* 181, 213; Reinke, *A.* 186, 286; Knuth, *A.* 186, 301; Langfurth, *A.* 191, 180; Bassmann, *A.* 191, 229, 238; Spiegelberg, *A.* 197, 266).

Formation.—1. From amido-benzene m-sulphonic acid and bromine.—2. From (1, 2, 4)-bromo amido benzene sulphonic acid and Br.—3. From the corresponding $C_6H_2Br_2(NO_2)SO_3H$.—4. From (1,3,5,2,6)-tribromo-nitro-benzene sulphonic acid, Sn, and HCl. 5. From tribromo-amido-benzene sulphonic acid by treating with water at 150°, or by treating with Sn and HCl.

Properties.—Needles (from hot water); sl. sol. water, insol. alcohol.

Reactions.—1. *Water* at 250° forms o-bromo-aniline sulphonic acid and aniline m-sulphonic acid.—2. *Diazo- reaction* gives (1,3,4)-di-bromo-benzene sulphonic acid. — 3. Warmed with

strong alcohol and KNO_2 a yellow crystalline body, possibly $C_6H_2Br_2(SO_3H).N_2H.C_6H_2Br_2SO_3K$, is formed. Heated in sealed tubes with alcohol, it splits up into dibromo-benzene sulphonic acid and amido-dibromo-benzene sulphonic acid (Bässmann).

Salts.—BaA'_2 6aq. S. (of BaA'_2) 2·99 at 7°; 3·12 at 9°; 3·9 at 23°.—KA'aq.—NH_4A'.—CaA'_2 2aq.—CaA'_2 5aq.—PbA'_2. S. 2·9 at 22·5°.

(1,2,4,5)-Di-bromo-amido-benzene sulphonic acid $C_6H_2Br_2(NH_2)(SO_3H)$ [1:2:4:5]. S. ·109 at 10°; ·153 at 24°. From (1,2,4)-di-bromo-benzene sulphonic acid by nitration and reduction (Spiegelberg, *A.* 197, 279). Trimetric tables; v. sl. sol. alcohol.—NH_4A' aq.—KA' 2aq.—BaA'_2 aq: S. (of BaA'_2) ·67 at 11°.—PbA'_2 aq: S. (of PbA'_2) ·11 at 11°.—CaA'_2 3aq.—CaA'_2 4aq.—AgA'. S. ·053 at 11°.

(1,3,4,5)-Di-bromo-amido-benzene sulphonic acid $C_6H_2Br_2(NH_2)(SO_3H)$ [1:3:4:5]. S. 3·13 at 10·5°. From amido-benzene *o*-sulphonic acid by bromination (Limpricht, *A.* 181, 198; *B.* 8, 1429), or from (1,3,5)-di-bromo-benzene sulphonic acid by nitration and reduction (Lenz, *A.* 181, 36). Trimetric tables (anhydrous) or 4-sided prisms (with aq). Converted by Br into tri-bromo-aniline.

Salts. KA'aq.—NaA'aq. S. (of NaA') 3·7 at 12°.—BaA'_2 1½aq. S. (of BaA'_2) ·20 at 11°.—PbA'_2 aq.

Di-bromo-amido-benzene sulphonic acid $C_6H_2Br_2(NH_2)(SO_3H)$ [1:4:2?:6]. S. ·62 at 10·5°. From (1,4,2)-di-bromo-benzene sulphonic acid by nitration and reduction (Borns, *A.* 187, 362). Needles or prisms.—KA'.—BaA'_2 aq.

Di-bromo-amido-benzene disulphonic acid $C_6HBr_2(NH_2)(SO_3H)_2$ [1:4:3?:2:6?]. From *p*-di-bromo-benzene disulphonic acid by nitration and reduction (Borns, *A.* 187, 367). Crystals; v. sol. water. K_2A''.—BaA''.

Di-bromo-amido-benzene di-sulphonic acid $C_6HBr_2(NH_2)(SO_3H)_2$. [1:4or6:2:3:5]. From (1,2,4)-amido-benzene disulphonic acid and Br (Heinzelmann, *A.* 188, 182). Prisms (containing 4aq); v. sol. water.—$(NH_4)_2A''$.—K_2A''.—BaA'' 8aq.—PbA'' 3aq.

Di-bromo-di-amido-benzene sulphonic acid $C_6HBr_2(NH_2)_2SO_3H$ [1:3:2:6:4]. One of the products of the reduction of $C_6Br_3(NH_2)_2SO_3H$ (Bässmann, *A.* 191, 244, 248). Tablets (containing aq), v. sl. sol. water.

Tri-bromo-amido-benzene sulphonic acid $C_6HBr_3(NH_2)SO_3H$, [1:3:5:4:6]. S. 13·7 at 14°, 16·6 at 7° (B.).

Formation.—1. From amido-benzene *m*-sulphonic acid and Br^6(Berndsen, *A.* 177, 86).—2. From the corresponding nitro-acid, by Sn and HCl, some di-bromo-amido-benzene sulphonic acid being also formed (Reneke, *A.* 186, 282; Knuth, *A.* 186, 298; Langfurth, *A.* 191, 198).—3. From (1,2,4)-bromo-amido-benzene sulphonic acid by bromination (Spiegelberg, *A.* 197, 275).

Properties.—Thin needles (containing aq). Sol. cold water and alcohol. Heated with water at 145° it becomes $C_6H_3Br_2(NH_2)SO_3H$.

Salts.—BaA'_2 9aq. S. (dry). ·43 at 7° (L.), ·34 at 3° (Bässmann, *A.* 191, 221).—KA'aq. ·935 at 4° (B.).—PbA'_2 9aq. S. (of PbA'_2) ·73 at 14°.

Tri-bromo-amido-benzene sulphonic acid $C_6HBr_3(NH_2)(SO_3H)$ [1:2:3:4:5]. From (1, 2, 3, 5)-tri-bromo-benzene sulphonic acid by nitration and reduction (Lenz, *A.* 181, 48). Tufts of slender needles (containing aq), v. sol. water and 95 p.c. alcohol.—BaA'_2 1½aq.

Tri-bromo-amido-benzene sulphonic acid $C_6HBr_3(NH_2)(SO_3H)$ [1:2:5:6:4]. From the corresponding nitro-acid (Spiegelberg, *A.* 197, 288). Long prisms (containing 1½aq) or slender needles (with aq). V. sol. water and alcohol.—KA'aq. S. (of KA') 2·09 at 1°.—NH_4A'.—CaA'_2 3½aq.—BaA'_2. S. ·096 at 1°.—PbA'_2 2aq. S. ·40 at 3·5°.—AgA' ½aq. S. (of AgA') ·46 at 10°.

Tri-bromo-di-amido-benzene sulphonic acid $C_6Br_3(NH_2)_2SO_3H$ [1:3:5:2:4:6]. A product of reduction of $C_6Br_3(NO_2)_2SO_3H$ (Bässmann, *A.* 191, 219).—BaA'_2 1½aq.

Tetra-bromo-amido-benzene sulphonic acid $C_6Br_4(NH_2)SO_3H$. [1:2:3:5:4:6]. S. 2·25 at 11° (Beckurts, *A.* 181, 223). Got by reducing $C_6Br_4(NO_2)SO_3H$ with Sn and HCl, not allowing the temperature to rise to 100°, or Br_2 will be displaced by H_2. Needles (containing 2aq). V. sol. alcohol and water.

Salts.—(Langfurth, *A.* 191, 204) BaA'_2 aq. S. (of BaA'_2) ·4 at 10°.—CaA'_2 7aq, KA' 1½aq. S. (of KA') 1·71 at 15°.

Tetra-bromo-amido-benzene sulphonic acid $C_6Br_4(NH_2)(SO_3H)$ [1:2:3:4:5:6]. S. ·03 at 11°. From the nitro acid (Spiegelberg, *A.* 197, 302). Needles (containing 2aq). V. sol. alcohol.—KA'aq. S. (of KA') ·106 at 11°.—CaA'_2 2aq. S. (of CaA'_2) ·107 at 11·5°.—BaA'_2 aq. S. (of BaA'_2) ·0155 at 11·5°.

(α)-BROMO-*o*-AMIDO-BENZOIC ACID $C_6H_3Br(NH_2)CO_2H$ [1:2:3]. *Bromo-anthranilic acid.* [170°]. From the corresponding nitro-compound by Sn and HCl (Hübner, *A.* 222, 104; *cf. A.* 143, 241; 149, 134). Needles; m. sol. water. Sodium amalgam reduces it to *o*-amido-benzoic acid [144°]. Nitrous acid forms the diazo-derivative $C_6H_3BrCO_2H.N_2.NH.C_6H_3BrCO_2H$.—Salts.—AgA'. BaA'_2 aq.—CuA'_2.

Acetyl derivative $C_6H_3Br(NHAc)(CO_2H)$ [1?:2:3]? [215°]. Obtained by brominating acetyl-*o*-amido-benzoic acid (Jackson, *B.* 14, 879).

(β)-Bromo-*o*-amido-benzoic acid. *Bromo-anthranilic acid.* $C_6H_3Br(NH_2)CO_2H$ [1:4:3]. [208°].

Formation.—1. By reducing (1, 4, 3)-bromo-nitro-benzoic acid (Hübner, Ohly a. Philipp, *A.* 143, 242; Mecker, Hubner a. Petermann, *A.* 149, 133).—2. By boiling bromo-isatoic acid with conc. HCl (Dorsch, *J. pr.* [2] 33, 35).

Properties.—V. sol. acetone, sol. alcohol, ether, chloroform, benzene, and glacial acetic acid, sl. sol. boiling water. Sodium-amalgam reduces it to *o*-amido-benzoic acid [144°].

Salts.—BaA'_2 4aq: needles, v. sol. water.

Amide. $C_6H_3Br(NH_2)CO.NH_2$. [177°]. From bromo-isatoic acid and NH_3Aq. Flat needles. V. sol. alcohol, acetone and glacial acetic acid, m. sol. water and benzene. Insol. ether.

(1,2,4)-Bromo-*m*-amido-benzoic acid $C_6H_3Br(NH_2)CO_2H$ [1:2:4]. [225°]. By reducing the nitro-acid by Sn and HCl. Small colourless needles (from water), becomes reddish in air (Hübner, *A.* 222, 179; Burghard, *B.* 8, 558; Raveill, *B.* 10, 1707). Reduced by sodium-amalgam to *m*-amido-benzoic acid.—HA'HCl.—CuA'_2.—PbA'_2.

(1,3,5)-Bromo-*m*-amido-benzoic acid $C_6H_3Br(NH_2)CO_2H$ [1:3:5]. [215°]. From the

corresponding nitro- acid by Sn and HCl (Hesemann a. Köhler, *A.* 222, 169). Needles (from alcohol). Turns red in light. Salts.—HA'HCl.—$(HA')_2H_2SO_4$.—BaA'_2 4aq.—CaA'_2 5½aq.

(1,4,2)-Bromo-*m*-amido-benzoic acid $C_6H_3Br(NH_2)CO_2H$ [1:4:2]. [180°]. From (1,4,2)-bromo-nitro-benzoic acid, Sn, and glacial HOAc (Burghard, *B.* 8, 560). Flat needles (Smith, *B.* 10, 1706).

(1,2,4,5)-Di-bromo-*o*-amido-benzoic acid $C_6H_2Br_2(NH_2).CO_2H$ [1:2or6:5:4]. *Di-bromo-anthranilic acid.* [226°–228°].

Formation.—1. From di-bromo-nitro-benzoic acid (Smith, *B.* 10, 1706).—2. From *o*-nitro-toluene and bromine at 170° (Wachendorff, *A.* 185, 281; Grieff, *B.* 13, 288).—3. From isatoic acid (*q.v.*) and bromine (Dorsch, *J. pr.* [2] 33, 37).

Properties.—Clumps of needles (from alcohol). Long needles (when sublimed). Sol. alcohol, acetone and glacial acetic acid, sl. sol. chloroform, benzene, ether, and water.

Amide $C_6H_2Br_2(NH_2)CO.NH_2$. [197°]. Pearly tablets (from alcohol-acetone). Formed from di-bromo-isatoic acid and NH_3,Aq at 100°.

Di-bromo-*o*-amido-benzoic acid $C_6H_2Br_2(NH_2)CO_2H$ [1:2or6:5:4]? *Di-bromo-anthranilic acid.* [225°]. S. 1; S. (alcohol) 2. From the nitro- acid by reduction (Hübner, *A.* 222, 189). Colourless needles. Reduced by sodium amalgam to *o*-amido-benzoic acid. BaA'_2 4aq. — CaA'_2 4½aq. — SrA'_2 2aq. — CuA'_2. This acid is probably identical with the preceding.

(1,3,4,5)-Di-bromo-*o*-amido-benzoic acid $C_6H_2Br_2(NH_2)CO_2H$ [1:3:4:5]. *Di-bromo-anthranilic acid.* [225°]. S. 1; S. (HOAc) 3. By reduction of the nitro- acid by Sn and HCl (Hesemann a. Köhler, *A.* 222, 175). Reduced by sodium amalgam to *o*-amido-benzoic acid. Needles (from alcohol).—BaA'_2 4aq.—CaA'_2 4aq. —CuA'_2.

(1,3,5,4)-Di-bromo-*o*-amido-benzoic acid $C_6H_2Br_2(NH_2)(CO_2H)$. *Di-bromo-anthranilic acid.* [196°]. From benzoic acid by bromination, nitration, and reduction (Angerstein, *A.* 158, 16). Needles (from dilute alcohol). Reduced by sodium-amalgam to *o*-amido-benzoic acid.

Di-bromo-*p*-amido-benzoic acid $C_6H_2Br_2(NH_2)CO_2H$ [1:3:2:5]. Obtained by adding bromine-water to an acidified solution of *p*-amido-benzoic acid (Beilstein a. Geitner, *Z.* [2] 1, 505; *A.* 139, 1). Needles (from alcohol). —NH_4A' 2aq.—NaA' 5aq. —CaA'_2 6aq.—BaA'_2 4aq.

Tri-bromo-*o*-amido-benzoic acid $C_6HBr_3(NH_2)CO_2H$ [1:2:x:4:5]. *Tri-bromo-anthranilic acid.* [c.119°]. From isatoic acid and bromine (Dorsch, *J. pr.* [2] 33, 37).

Properties.—Slender needles. May be sublimed. Very soluble in glacial acetic acid, alcohol and acetone, sol. ether and chloroform, less soluble in benzene, sl. sol. hot water.

Tri-bromo-*m*-amido-benzoic acid $C_6HBr_3(NH_2)CO_2H$ [1:3.5:4:6]. [170°]. From *m*-amido-benzoic acid and bromine-water (Beilstein a. Geitner, *Z.* [2] 1, 505; *A.* 139, 6; Vollbrecht, *B.* 10, 1708). Needles; m. sol. hot water. On dry distillation it gives tri-bromo-aniline.—NaA' 4aq.—BaA'_2 6aq.

Tri-bromo-di-amido-benzoic acid $C_6Br_3(NH_2)_2(CO_2H)$ [1:3:5:2:4:6]. From *s*-di-amido-benzoic acid and bromine-water (Griess, *A.* 154, 332). Long needles (from dilute alcohol). Sl. sol. cold water.—AgA'.

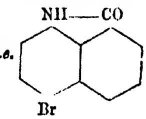
Tetra-bromo-*o*-amido-benzoic acid $C_6Br_4(NH_2)CO_2H$ [1:2:3:4:5:6]. [115°]. From isatoic acid and excess of Br (in glacial acetic acid) (Dorsch, *J. pr.* [2] 33, 38). White needles. At 100° it sublimes in long slender needles.

BROMO-AMIDO-HYDROCARBOSTYRIL *v.* p. 164.

BROMO-AMIDO-HYDROCINNAMIC ACID *v.* BROMO-AMIDO-β-PHENYL-PROPIONIC ACID.

BROMO-AMIDO-NAPHTHALENE *v.* BROMO-NAPHTHYLAMINE.

BROMO-AMIDO-NAPHTHOIC ANHYDRIDE

$C_{11}H_6ONBr$ *i.e.*  *Bromo-naphthostyril.* [257°]. By reduction of bromo-nitro-(α)-naphthoic acid with $FeSO_4$ and aqueous NH_3 and ppn. with acetic acid the amido- acid is obtained, and by boiling with alcohol it is converted into the anhydride, which crystallises out on cooling in brown needles (Ekstrand, *B.* 19, 1136).

Di-bromo-amido-naphthoic anhydride $C_{10}H_4Br_2\Big<\begin{array}{l}CO\\ \mid\\ NH\end{array}$. *Di-bromo-naphthostyril.* [270°]. Prepared by heating amido-naphthoic anhydride $C_{10}H_6\Big<\begin{array}{l}CO\\ \mid\\ NH\end{array}$ suspended in water with a large excess of bromine. Yellow needles (from alcohol). M. sol. hot acetic acid.

Acetyl derivative $C_{11}H_4ONBr_2Ac$ [185°]; small yellow needles (Ekstrand, *B.* 19, 1136).

BROMO-AMIDO-(α)-NAPHTHOQUINONE $C_6H_4\Big<\begin{array}{l}CO.C(NH_2)\\ CO.CBr\end{array}$. [205°]. Formed by boiling bromo-amido-(α)-naphthoquinone-imide $C_6H_4\Big<\begin{array}{l}CO - C(NH_2)\\ \quad\quad\ \ \Vert\\ C(NH).CBr\end{array}$ with dilute acids. Orange silky needles. Sublimable. By boiling with dilute alkalis it is converted into bromo-oxy-(α)-naphthoquinone.

Acetyl derivative: [157°]; sulphur-yellow needles (Zincke a. Gerland, *B.* 20, 1514).

BROMO-AMIDO-(α)-NAPHTHOQUINONE-IMIDE $C_6H_4\Big<\begin{array}{l}CO\ \ C(NH_2)\\ \quad\quad\ \ \Vert\\ C(NH).CBr\end{array}$. [200°]. Obtained by adding bromine (5 c.c.) to di-amido-(α)-naphthol or its stanno-chloride (10 g.) suspended in acetic acid. Orange-yellow needles (from alcohol). V. sol. hot alcohol and hot benzene. By $SnCl_2$ it is reduced to bromo-di-amido-(α)-naphthol. By boiling with dilute acids it is converted into bromo-amido-(α)-naphthoquinone $C_6H_4\Big<\begin{array}{l}CO.C(NH_2)\\ \quad\quad\ \Vert\\ CO.CBr\end{array}$. By boiling with dilute NaOH it is converted into bromo oxy-naphthoquinone-imide $C_6H_4\Big<\begin{array}{l}CO - C(OH)\\ \quad\quad\ \ \Vert\\ C(NH).CBr\end{array}$. The latter body

when treated with conc. HCl or alcoholic NaOH is converted into bromo-oxy-naphthoquinone $C_6H_4<\begin{smallmatrix}CO.C(OH)\\CO.CBr\end{smallmatrix}$ which is also formed by boiling the bromo-amido-naphthoquinone with dilute alkalis (Zincke a. Gerland, *B.* 20, 1510).

BROMO-o-AMIDO-PHENOL

$C_6H_3Br(NH_2)(OH)$ [1:3:4]. [128°]. Formed by reducing bromo-nitro-phenol with Sn and HCl (F. Schütt, *J. pr.* [2] 32, 61). Thin plates (from CS_2). Needles (from alcohol). Sol. ether, benzene, hot water, and hot chloroform. Fe_2Cl_6 turns the aqueous solution cherry-red.

Salts.—B'HCl*. Very soluble plates.—B'HBr*. Crystallises very easily.—$B'_2H_2SO_4$.

Acetyl derivative $C_6H_3(OH)(NHAc)Br$. [178°]. Plates or needles (from water).

Methyl ether $C_6H_3Br(NH_2)(OMe)$. [98°]. From the nitro- compound, Sn and HCl (Staedel, *A.* 217, 59). Plates (from benzene). V. sol. benzene, ether or hot alcohol, insol. water. Salts.—B'HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Ethyl ether [57°]. Broad needles (from alcohol). V. sol. benzene, alcohol or ether. *Salts.*—B'HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Bromo-*m*-amido-phenol $C_6H_3Br(NH_2)OH$ [x:1:3]. *Ethyl ether* $C_6H_3Br(NH_2)OEt$. Liquid; v. sol. alcohol and ether, v. sl. sol. water. The hydrochloride, sulphate, and oxalate crystallise in white plates $C_6H_3Br(OEt)NH_2$, HCl, $SnCl_2$ (Lindner, *B.* 18, 612).

Bromo-*p*-amido-phenol

$C_6H_3Br(NH_2)(OH)$ [1:3:6]. [158°]. Prepared by reducing bromo-nitro-phenol, or its benzyl derivative, by Sn and HCl (O. Hölz, *J. pr.* [2] 32, 65). Short needles (from dilute alcohol). Sol. ether, benzene, and chloroform, sl. sol. cold water.

Salts. — B'HCl: silvery plates.—(B',HCl) $SnCl_2$.—B'HBr.

Acetyl derivative $C_6H_3(OH)(NHAc)Br$. [157°]. Thick needles (from hot water). Soluble in alkalis.

Methyl ether.

From the nitro-compound, Sn and HCl (Staedel, *A.* 217, 68). Oil. Insol. water, v. sol. benzene, alcohol, or ether. B'HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Ethyl ether

From the nitro-compound, Sn and HCl. Oil. B'HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Di-bromo-o-amido-phenol

$C_6H_2Br_2(NH_2)(OH)$ [1:3:5:6]. [92°]. Formed by reducing di-bromo-*o*-nitrophenol (Hölz, *J. pr.* [2] 32, 69). Slender yellow needles (from dilute alcohol). Sparingly soluble in water, v. sol. alcohol, ether, benzene, and chloroform.

Salts. - B'HCl: plates. — $(B'HCl)_2SnCl_2$: needles.- B'HBr: needles.

Acetyl derivative $C_6H_2(OH)(NHAc)Br_2$. [186°]. Yellowish needles (from hot water). Sol. alkalis.

Methyl ether $C_6H_2Br_2(NH_2)(OMe)$. From the nitro- compound by Sn and HCl (Staedel, *A.* 217, 63). Oil. Sol. alcohol, ether, or dilute acids, insol. cold water, sl. sol. hot water. B'HCl.—$B'_2H_2SO_4$. [177°].—$B'_2H_2C_2O_4$.

Ethyl ether $C_6H_2Br_2(NH_2)(OEt)$. [92°]. Quadratic crystals (from alcohol). V. sol. alcohol or ether. - B'HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Di-bromo-o-amido-phenol.

Ethyl ether $C_6H_2Br_2(NH_2)OEt$ [1:3:4:5]? [53°]. *o*-Amido-phenetol, $C_6H_4(NH_2)OEt$ (10 g.), boiled with glacial acetic acid (100 g.) and bromin (11·7 g.). The product is poured into water an the oil that separates is distilled with steam an recrystallised from alcohol. Glittering prisms grouped in tufts. Resembles di-bromo-*o*-toluidine in being but feebly basic (Möhlau a. Oehmichen. *J. pr.* 132, 479).

Di-bromo-*m*-amido-phenol.

Ethyl ether $C_6H_2Br_2(NH_2)OEt$. From the nitro- compound. Oil. The hydrochloride, sulphate, and oxalate crystallise in needles.—$C_6H_2Br_2(OEt)NH_2$,HCl,$SnCl_2$: glistening plates (Lindner, *B.* 18, 613).

Di-bromo-*p*-amido-phenol.

$C_6H_2Br_2(NH_2)OH$ [1:3:5:2]. [180°] (M. a. B.); [190°] (L. a. G.). Formed by reducing the nitro- compound (Möhlau, *B.* 16, 2845; Hölz, *J. pr.* [2] 32, 67; Möhlau a. Böhmer, *J. pr.* [2] 24, 470; Lellmann a. Grothmann, *B.* 17, 2731). Formed also by reducing di-brominated *p*-diazophenol (*q. v.*) with tin and HCl (Böhmer, *J. pr.* 132, 469):

$$C_6H_2Br_2<\begin{smallmatrix}O\\N_2\end{smallmatrix} + 2H_2 = C_6H_2Br_2(OH).NH_2 + NH_3.$$

Properties.—Ppd. by $NaHCO_3$ from solution of its hydrochloride as microscopically small needles grouped in tufts. Turns blue in air. Sl. sol. ether, v. sol. alcohol, m. sol. hot water.

Salts. — B'HCl: glittering plates.—$(B'HCl)_2SnCl_2$.—B'HBr.

Reactions.—When N_2O_3 is passed into an alcoholic solution of its hydrochloride, yellow crystals of diazo-dibromo-phenol (*q. v.*) are obtained, but this body is *isomeric* with that by the reduction of which the dibromo-amido-phenol was prepared. An 'intra-molecular change' must therefore have occurred somewhere.

Acetyl derivative $C_6H_2Br_2(NHAc)(OH)$. [174°]. Glittering plates (from dilute alcohol).

Methyl ether From the nitro- compound [127°], Sn, and HCl. White porcelain-like mass. Extremely sol. ether, benzene, or alcohol (Staedel, *A.* 217, 70; Staedel a. Damm, *B.* 11, 1749). Salts.—B'HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$ [195°].

Ethyl ether [67°]. Needles (from alcohol). V. sol. alcohol, ether, or benzene. Salts.—B'HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Tri-bromo-o-amido-phenol.

Ethyl ether $C_6HBr_3(NH_2)OEt$ [1:3:4:5:6]? [77°]. From amido-phenetol (5 g.), glacial acetic acid (50 g.) and bromine (17·5 g.). The product is poured into water, and the pp. crystallised from alcohol. Long silky needles. Nearly insol. boiling conc. HCl. It is totally decomposed when heated to a temperature a little above its melting-point.

Tri-bromo-*m*-amido-phenol

$C_6HBr_3(NH_2).OH$ [1:3:5:2:6]. [115°]. Formed by reduction of tri-bromo-*m*-nitro-phenol (Daccomo, *B.* 18, 1168). Colourless silky needles. Sol. alcohol, ether, benzene, and hot, sl. sol. cold, water. Fe_2Cl_6 gives a green colouration.

Ethyl ether $C_6HBr_3(NH_2)OEt$. Solid, v. sol. alcohol and ether, sl. sol. water.—B'HCl: white needles, sol. alcohol.—$B'_2H_2SO_4$: white needles, sol. alcohol. — B'HClSnCl$_2$: white needles (Lindner, *B.* 18, 614).

BROMO-AMIDO-DIPHENYL.

Acetyl derivative $C_{12}H_8BrNHAc$. [247°]. From Br and *p*-amido-diphenyl in ...

HOAc (Hübner, *A.* 209, 345). Needles (from alcohol).

Di-bromo-di-amido-diphenyl $C_{12}H_6Br_2(NH_2)_2$. [89°]. From di-bromo-di-nitro-diphenyl by Sn and HCl (Fittig, *A.* 132, 207). Insol. water.—B″2HCl.

Di-bromo-di-amido-diphenyl [2:4:1] $C_6H_3Br(NH_2).C_6H_3Br(NH_2)$ [1:2:4]. *Di-bromo-benzidine.* [152°]. Obtained from [3:1] $C_6H_4Br.NH.NH.C_6H_4Br$ [1:3] and HCl (Gabriel, *B.* 9, 1407). Trimetric crystals, m. sol. cold alcohol.—B″2HCl.—B″H_2PtCl_6.

Di-bromo-di-amido-diphenyl $C_{12}H_6Br_2(NH_2)_2$ [1:5:2]₂. [108° corr.]. Small plates. Formed by the action of an alcoholic solution of $SnCl_2$ and H_2SO_4 on *p*-bromo-benzene-*p*-azo-bromo-benzene. Treated with nitrous acid in alcoholic solution it gives an azimido-body $C_{12}H_6N_3Br_2$ which forms glistening violet needles, [206°], sl. sol. alcohol (Schultz, *B.* 17, 465).

Tetra-bromo-di-amido-diphenyl $C_{12}H_8Br_4N_2$. *Tetra-bromo-benzidine.* [286°]. Prepared by bromination of benzidine (Claus a. Risler, *B.* 14, 86). Slender colourless needles. Sol. alcohol, ether, CS_2, C_6H_6; insol. water and acids.

BROMO-AMIDO-PHENYL-ACETIC ACID $C_6H_3(Br)(NH_2)(CH_2.CO_2H)$[1:2:5]. [136°]. Formed by saponification of the acetyl derivative of its nitrile, or by bromination and saponification of the acetyl derivative of *p*-amido-phenyl-acetic acid (Gabriel, *B.* 15, 840). Colourless plates. Sol. alcohol and ether, insol. CS_2.

Acetyl derivative [165°].

Nitrile $C_6H_3(Br)(NH_2)(CH_2CN)$. *Acetyl derivative* $C_6H_3Br(NHAc)(CH_2CN)$ [129°]. Long colourless needles. Sol. alcohol, sl. sol. cold water. Formed by bromination of the acetyl derivative of *p*-amido-phenyl-acetonitrile (Gabriel, *B.* 15, 840).

Bromo-amido-phenyl-acetic acid $C_6H_3Br(NH_2)CH_2.CO_2H$ [1:2 or 6:4]. [134°]. From the nitro-compound [114°] by Sn and HCl (P.P. Bedson, *C. J.* 37, 98). Silky needles (from water). Sol. alcohol and $CHCl_3$. Sl. sol. ether.—B′HCl aq: turns red in air.

(α)-Bromo-amido-phenyl-acetic acid $C_6H_3Br(NH_2)CH_2.CO_2H$. [167°]. From the nitro-acid [169°] by Sn and HCl (Bedson). White needles (from water), reddens in air. Sol. alcohol and chloroform, sl. sol. ether.

Salt.—B′HClaq: white needles (from water).

(β)-Bromo-amido-phenyl-acetic acid $C_6H_3Br(NH_2)CH_2.CO_2H$. [186°]. From the nitro-acid [162°] by Sn and HCl (Bedson). The hydrochloride is less soluble in water than those of the two preceding bodies.

(1, 3, 2, 5)-Bromo-di-amido-phenyl-acetic acid $C_6H_2(Br)(NH_2)_2.CH_2.CO_2H$ [1:3:2:5]. [c. 200°]. Long colourless needles. Formed by reduction of (1, 3, 2, 5)-bromo-nitro-amido-phenyl-acetic acid (Gabriel, *B.* 15, 1995).

BROMO-AMIDO-PHENYL-ETHANE $C_8H_{10}BrN$ *i.e.* $C_6H_4Br.CH_2.CH_2.NH_2$. *Bromo-phenyl-ethyl-amine* (253°). From phenyl-propionamide, KOHAq, and bromine (Hofmann, *B.* 18, 2740). Pearly plates (from water).—B′HCl.

(1,2,5) BROMO-AMIDO-β-PHENYL-PROPIONIC ACID $C_6H_3(Br)(NH_2).C_2H_4.CO_2H$ [1:2:5]. *Bromo-amido-hydrocinnamic acid* [105°]. Formed by bromination of the acetyl derivative of *p*-amido-phenyl-propionic acid, and saponification of the product (Gabriel, *B.* 15, 2292). Long glistening crystals. Sol. most ordinary solvents and in acids and alkalis.

Acetyl derivative: [160°]. Long colourless needles, soluble in alcohol, ether, and benzene.

Bromo-*m*-amido-phenyl-propionic acid $C_6H_3(Br)(NH_2).C_2H_4.CO_2H$ [2:1:5]. [117°-119°]. Long prisms. Sol. water, alcohol, ether, and C_6H_6. Prepared by reduction of *p*-bromo-*m*-nitro-hydrocinnamic acid with tin and HCl.—A′HCl: glistening soluble needles (Gabriel a. Zimmermann, *B.* 13, 1681).

(*eso*)-DI-BROMO-*o*-AMIDO-PHENYL-VALERIC ACID $C_6H_2Br_2(NH_2).CH_2.CH_2.CH_2.CH_2.CO_2H$. [96°, with aq]. Long colourless needles (containing aq). Formed by reduction of an alcoholic solution of di-bromo-amido-phenyl-di-bromo-valeric acid $C_6H_2Br_2(NH_2).CHBr.CHBr.CH_2.CH_2.CO_2H$ with zinc and HCl. V. sol. ordinary solvents, insol. cold water. It could not be converted into an inner anhydride, even by dehydrating agents.

Ethyl ether $C_{10}H_{10}Br_2(NH_2)CO_2Et$; thick oil; its hydrochloride forms white needles [136°].

Acetyl derivative $C_{10}H_{10}Br_2(NHAc)CO_2H$ [206°]; aggregates of thin white needles; v. sol. alcohol, ether, &c.

Acetyl-ethyl-ether $C_{10}H_{10}Br_2(NHAc)CO_2Et$ [139°]; colourless crystals; v. sol. alcohol, ether, and acetic acid, more sparingly in benzene, insol. water and ligroïn; in small quantities it can be distilled undecomposed (Diehl a. Einhorn, *B.* 20, 380).

δγ-*eso*-Tetra-bromo-*o*-amido-phenyl-valeric acid $C_6H_2Br_2(NH_2).CHBr.CHBr.CH_2.CH_2.CO_2H$. [167°]. Formed by bromination of *o*-amido-styryl-propionic acid dissolved in chloroform. Small microscopic needles. V. sol. alcohol, ether, and acetic acid, insol. water and CS_2 (Diehl a. Einhorn, *B.* 20, 379).

BROMO-AMIDO-QUINOLINE $C_9H_5N(Br)(NH_2)$. [164°]. Large monoclinic prisms, or long colourless needles (containing aq). Sol. alcohol and ether.

Salts.—B′HNO_3: glistening yellow needles.—B′HCl: soluble red prisms.—B′$_2H_2Cl_2PtCl_4$: microscopic orange needles.

Acetyl derivative $C_9H_5N(Br)(NHAc)$. [105°]. Thin colourless plates (La Coste, *B.* 15, 1920).

DI-BROMO-AMIDO-RESORCIN $C_6HBr_2(NH_2)(OH)_2$ [1:2:4]. *Di-ethyl ether* $C_6HBr_2(NH_2)(OEt)_2$ [112°]; glistening needles or plates (Will a. Pukall, *B.* 20, 1126).

BROMO-AMIDO-STYRENE $C_6H_3Br(NH_2).C_2H_3$.

Acetyl derivative [183°]; felted needles, sol. alcohol, ether, and acetic acid; formed by bromination of *p*-amido-cinnamic acid dissolved in AcOH (Gabriel a. Herzberg, *B.* 16, 2043).

BROMO-AMIDO-SUCCINIC ACID $C_2H_2Br(NH_2)(CO_2H)_2$. [140°]. From di-bromo-succinic acid and alcoholic NH_3 (Claus, *B.* 15, 1850). Radiating needles; v. sol. water and alcohol.—AgA′.

BROMO-AMIDO-THYMOL $C_6HBr.MePr(NH_2)(OH)$. Prepared by adding Na_2CO_3 to dilute solution of its hydrobromide (*v. infra*). Long colourless prisms, rapidly turning deep violet.

... —HBr. By adding moderately strong HBr to thymoquinone-chloro-imide (*q. v.*) a yellow flocculent pp. is formed. Ether extracts bromo-thymoquinones from this, leaving the above salt, which is soluble in water and alcohol, but is thrown down as needles when HBr is added to its concentrated aqueous solution (Andresen, *J. pr.* 131, 182).

Bromo-amido-thymol [c. 90°]. From bromo-nitro-thymol, zinc-dust, and HCl (Mazzara a. Discalzo, *G.* 16, 196). Scales. Converted by nitrous acid gas into bromo-thymoquinone [48°].

BROMO-AMIDO-TOLUENE *v.* BROMO-TOLUIDINE.

Bromo-di-amido-toluene *v.* BROMO-TOLYLENE DIAMINE.

BROMO - AMIDO - TOLUENE SULPHONIC ACID $C_6H_2(CH_3)(NH_2)BrSO_3H$ [1:2:3:5]. *Bromo-toluidine sulphonic acid.* From *o*-toluidine sulphonic acid and bromine-water (Nevile a. Winther, *C. J.* 37, 627). Prisms.

Reactions.—1. Converted by diazo- reaction into a bromo-toluene sulphonic acid whose sulphochloride melts at [56°] and whose amide at [147°].—2. Heated with HCl at 160° it gives dibromo-*o*-toluidine [44°] and two mono-bromo-toluidines, an oil and a crystalline body, [54°-57°]. One of these bromo-toluidines must be obtained from the acid by displacement of SO_3H by H, and must subsequently give rise to the other mono- and the di-bromo toluidine. Inasmuch as oily bromo-toluidine, $C_6H_3Me(NH_2)Br$ [1:2:3], heated with HCl at 160° gives a substance [40°-47°] and crystals [53°-55°], while the crystalline bromo-toluidine [54°-57°] is not affected by this treatment, we must suppose the sulphonic acid to be $C_6H_2(CH_3)(NH_2)BrSO_3H$ [1:2.3:5] rather than [1:2:5:3]. When it is heated with HCl the oily bromo-toluidine is first formed, but this being unstable changes into its crystalline isomeride and the crystalline dibromo-toluidine.

Bromo-amido toluene sulphonic acid $C_6H_2Me(NH_2)Br(SO_3H)$ [1:4:2:3 or 5]. S. ·532 at 21°. From *o* bromo toluene by sulphonation, nitration, and reduction (Schäfer, *A.* 174, 360). Trimetric laminæ (from hot water) or nodules (from alcohol). Converted by bromine-water into tri-bromo-toluidine [82°].

Salts. BaA'_2aq. PbA'_2aq.

Bromo-amido-toluene sulphonic acid $C_6H_2Me(NH_2)Br(SO_3H)$. [1:5?:4:3]. From (1,4,2)-bromo-toluene sulphonic acid by nitration, and reduction (S.). Needles (from water). V. sl. sol. water.—BaA'_2 4aq.

Bromo-amido-toluene sulphonic acid $C_6H_2Me(NH_2)Br(SO_3H)$ [1:2?:4:6]. S. 3·2. From (1,4,3)-bromo toluene sulphonic acid by nitration and reduction (Schäfer, *A.* 174, 360). Prisms (from water). Bromine-water gives tri-bromo-toluidine [72°].—BaA'_2 2aq.—NaA'_2 2aq.

Bromo-amido-toluene sulphonic acid $C_6H_2Me(NH_2)Br(SO_3H)$ [1:4:*x*:2]. S. ·23 at 20°. From boiling aqueous *p*-toluidine *o*-sulphonic acid and bromine (Jenssen, *A.* 172, 230; *B.* 7, 55). Needles (from water). V. sl. sol. boiling water.—KA′aq.—BaA'_2 7aq.

Bromo amido-toluene sulphonic acid $C_6H_2Me(NH_2)Br(SO_3H)$. S. ·19 at 20°. From *o*-toluidine sulphonic acid by conversion into *o*-bromo toluene sulphonic acid, nitration, and reduction (Pagel, *A.* 176, 300). Minute thin prisms.—BaA'_2 aq.

Bromo-amido-toluene sulphonic acid $C_6H_2Me(NH_2)Br(SO_3H)$ [1:4:5?:3]. Formed, together with di-bromotoluidine, by passing bromine-vapour into cold aqueous *p*-toluidine *m*-sulphonic acid (v. Pechmann, *A.* 173, 210; Limpricht, *B.* 7, 452). Clumps of needles. V. e. sol. water. Converted by diazo- reaction into (3 or 5, 1, 2) bromo-toluene sulphonic acid.—KA′.—BaA'_2 2aq.—PbA'_2.—AgA′.

Di-bromo-*o*-amido-toluene sulphonic acid $C_6HMe(NH_2)Br_2SO_3H$ [1:2:?:?:4]. S. ·64 at 13·5°. From *o*-toluidine *p*-sulphonic acid $C_6H_3Me(NH_2)(SO_3H)$ [1:2:4] and bromine (Hayduck, *B.* 7, 1353; *A.* 172, 211). Capillary needles containing aq (from water).—BaA'_2 9aq.

Di-bromo-amido-toluene sulphonic acid $C_6HMe(NH_2)Br_2(SO_3H)$ [1:2:3?:?:5?]. From *o*-toluidine by sulphonation and bromination. Needles (containing aq). V. sol. hot water and hot alcohol. Gives tri-bromo-toluidine [112°] when distilled with KOH.—BaA'_2 4aq.—PbA'_2 3aq (Gerver, *A.* 169, 380).

Bromo-di-amido-toluene sulphonic acid $C_6HMe(NH_2)_2BrSO_3H$ [1:2?:6?:3?:4]. From toluene *p*-sulphonic acid by nitration and reduction (Schwanert, *A.* 186, 360). Tables; sl. sol. water.—KA′2½aq.

DI-BROMO-AMYL ALCOHOL $C_5H_{10}Br_2O$ *i.e.* $CH_2Br.CHBr.CHEt.OH$. *Di-bromo-di-ethyl-carbinol.* From vinyl-di-ethyl-carbinol and bromine (Wagner, *J. R.* 16, 320). Non-volatile liquid.

BROMO-*o*-AMYL-ANTHRACENE

$$C_{19}H_{19}Br \text{ i.e. } C_6H_4\left\langle\begin{array}{c} C(C_5H_{11}) \\ | \\ CBr \end{array}\right\rangle C_6H_4.$$ [76°]. Yellow needles. Fluorescent. Prepared by bromination of amyl-anthracene in CS_2.

Picric acid compound. [110°]. Orange-yellow needles (Liebermann a. Tobias, *B.* 14, 797).

BROMO-*sec*-AMYL-BENZENE $C_{11}H_{15}Br$ *i.e.* $C_6H_5.CHEt.CHBr.CH_3$(?). (c. 79°) at 40 mm. S.G. [21] 1·28. Oil. Obtained by brominating *sec*-amyl-benzene (Dafert, *M.* 4, 620). Decomposed slowly by boiling water into HBr and pentenyl-benzene.

γ-δ-di-bromo-amyl-benzene [53°-54°] $Ph.CHBr.CHBr.CH_2.CH_2.CH_3$. From phenyl-amylene (*q. v.*) and bromine. Needles or plates.

γ-δ-di-bromo-isoamyl-benzene $Ph.CHBr.CHBr.CH(CH_3)_2$. [128°-129°]. From phenyl-iso-amylene and Br (Schramm, *A.* 218, 391). Needles (from alcohol).

Tri-bromo-isoamyl-benzene $C_{11}H_{13}Br_3$. [140°]. Obtained by brominating iso-amyl-benzene at 100° (Bigot a. Fittig, *A.* 141, 161). Needles.

BROMO-ISOAMYLENE C_5H_9Br. *Pentenyl-bromide.* (100°-110°). From 'isoamylene' by successive treatment with bromine and alcoholic KOH (Bauer, *A.* 120, 167). Successive treatment with conc. H_2SO_4 and water forms amylene dibromide and a ketone $C_5H_{10}O$ (Bouchardat, *C. R.* 93, 316).

ω-Bromo-iso-amylene (111°) Pr.CH:CHBr. From isovaleric aldehyde by successive treatment with PCl_3Br_2 and alcoholic KOH (Bruylants, *B.* 8, 406).

γ-Bromo-*n*-amylene $CH_2:CBr.CH_2.CH_2.CH_3$. (123°). S.G. [0] 1·10. From methyl propyl ketone

by successive treatment with PCl_3Br_2 and alcoholic KOH (B.).

Bromo-amylene C_5H_9Br. (111°). From di-bromo-hexoic acid $CH_3.CHBr.CBrEt.CO_2H$ and cold aqueous Na_2CO_3 (Fittig, *A.* 200, 36).

Bromo-amylene C_5H_9Br. (115°). From iso-valerylene and HBr (Reboul, *Z.* 1867, 173).

Bromo-amylene C_5H_9Br. (c. 106°). S.G. $\frac{15}{}$ 1·173. From isoprene C_5H_8 and HBr (Bouchardat, *J.* 1879, 577).

Di-bromo-amylene $C_5H_8Br_2$. (c. 170°). From isovalerylene and bromine (Reboul, *A.* 135, 372).

Di-bromo-amylene $C_5H_8Br_2$ *i.e.* Pr.CBr:CHBr. (175°). From isopropyl-acetylene and Br (Bruylants, *B.* 8, 407).

Di-bromo-amylene $C_5H_8Br_2$ *i.e.* Pr.CBr:CHBr. (190°). From *n*-propyl-acetylene and Br (B.).

BROMO-AMYLENE GLYCOL $C_5H_9Br(OH)_2$. From amylene dibromide by successive treatment with AgOAc and solid KOH (Bauer, *J.* 1861, 661).

TRI-BROMO-*p*-ISOAMYL-TOLUENE $C_{12}H_{15}Br_3$ *i.e.* $C_6HMeBr_3.C_5H_{11}$. From *p*-isoamyl-toluene and bromine at 100°. Sticky liquid (Bigot a. Fittig, *A.* 141, 165).

TRI-BROMO-ANETHOL $C_{10}H_9Br_3O$. From anethol and Br. Crystals (Cahours, *A.* 41, 60).

BROMO-ANILIC ACID *v.* DI-BROMO-DI-OXY-QUINONE.

o-**BROMO-ANILINE** C_6H_6BrN *i.e.* $C_6H_4Br(NH_2)$ [1:2]. Mol. w. 172. [31°]. (229° i. V.). From *o*-bromo-nitro-benzene by reduction with tin and HCl (Fittig a. Mager, *B.* 7, 1175).

Acetyl derivative $C_6H_4BrNHAc$. *o-Bromo-acetanilide.* [99°]. Long needles (Körner, *G.* 4, 330).

m-**Bromo-aniline** $C_6H_4Br(NH_2)$ [1:3]. [18°]. (251°). *Formation.*—1. From *m*-bromo-nitro-zene (Fittig a. Mager, *B.* 8, 361).—2. *m*-nitro-diazo-benzene sulphate (from *m*-nitraniline) is treated with a hot solution of cuprous bromide and the crude *m* bromo-nitro-benzene reduced with tin and HCl (Sandmeyer, *B.* 18, 1495).

Acetyl derivative $C_6H_4BrNHAc$. [88°]. Needles (from dilute alcohol) (Scheufelen, *A.* 231, 175).

p-**Bromo-aniline** $C_6H_4Br(NH_2)$ [1:4]. [62°]. (Mills, *P. M.* [5] 14, 27). [66°] (Körner, *J.* 1875, 342).

Formation.—1. By reducing *p*-bromo-nitro-benzene with tin and HCl (Riche a. Bérard, *A.* 133, 52; Fittig a. Mager, *B.* 7, 1175; 8, 361).—2. By bromination of acetanilide and distillation of the product with KOH (Mills, *P. M.* [4] 19, 21; *Pr.* 10, 589).—3. By distilling bromo-isatin with KOH (Hofmann, *A.* 53, 42).—4. In small quantity by brominating aniline with Br vapour or in benzene solution (Kekulé, *Z.* 1866, 387).

Properties.—Trimetric crystals; insol. cold water, v. sol. alcohol and ether. Decomposed on boiling, giving aniline, and di- and tri-bromo-aniline.

Reactions.—1. HCl at 160° gives aniline and di-bromo-aniline (Fittig a. Buchner, *A.* 188, 23). 2. *Sodium* acts on it in ethereal solution forming benzene-azo-benzene, aniline, and NaBr (Anschütz a. Schultz, *B.* 9, 1398; Claus a. Roques, *B.* 16, 909).—3. By dissolving in cooled fuming HNO_3 it is converted into tri-nitro-aniline (picramide) (Hager, *B.* 18, 2578).—4. By nitration of *p*-bromaniline dissolved in 10 pts. of H_2SO_4 bromo-nitro-aniline $C_6H_3Br(NO_2)(NH_2)$ [4:3:1] is produced (Nölting a. Collin, *B.* 17, 266).—5. *Cyanogen* forms a compound $C_6H_4Br.NH.C(NH).C(NH).NHC_6H_4Br$ [245°]; white plates (from alcohol) (Senf, *J. pr.* [2] 35, 530).

Salts.—B'HCl: monoclinic.—$B'_2H_2PtCl_6$.—B'HBr aq: monoclinic prisms (Staedel, *B.* 16, 28).—$B'_2H_2SO_4$: laminæ.—$B'_2H_2C_2O_4$.

Formyl derivative $C_6H_4Br.NH(CO.H)$. [119°]. Long white needles. Insol. cold water, sl. sol. hot water, v. sol. alcohol and ether. Prepared by heating *p*-bromaniline with formic ether, or by brominating formanilide (Dennstedt, *B.* 13, 234).

Thioformyl derivative $C_6H_4Br.NH(CS.H)$ [190°]. Needles. V. sol. hot ether and alcohol. Prepared by the action of P_2S_5 on the preceding body (Dennstedt, *B.* 13, 236).

Acetyl derivative [166°]. From acetanilide in glacial HOAc and Br (Remmers, *B.* 7, 346; Gärke, *B.* 8, 1114). Also from *p*-bromo-aniline and AcCl (Körner, *G.* 4, 329), or acetamide (Kelbe, *B.* 16, 1200). Monoclinic prisms: $a:b:c$ = 1·538:1:1·435 (Panebianco, *G.* 9, 357). M. sol. alcohol, v. sl. sol. water.

Isobutyryl derivative $C_6H_4Br.NH.C_4H_7O$. [128°]. From isobutyryl-aniline and Br vapour (Norton, *Am.* 7, 117). Needles (from alcohol).

Benzoyl derivative $C_6H_4Br(NHBz)$. [202°]. From benzanilide and Br (Meinecke, *B.* 8, 564).

Oxalyl derivative $C_2O_2(NH.C_6H_4Br)_2$. [above 200°]. From Br and oxanilide in HOAc (Dyer a. Mixter, *Am.* 8, 351).

Di-bromo-aniline $C_6H_3Br_2(NH_2)$ [1:3:4]. [79°]. *Formation.*—1. By saponifying dibrominated acetanilide (Griess, *A.* 121, 266), or brominated *o*- or *p*-bromo-acetanilide (Körner, *G.* 4, 329).—2. Together with mono- and tri-bromo-aniline by brominating aniline (Kekulé, *K.* 2, 635).—3. By distilling di-bromo-isatin with KOH (Hofmann, *A.* 53, 47).—4. Together with mono- and tri-bromo-aniline by heating nitrobenzene with conc. HBrAq at 190° (Baumhauer, *B.* 2, 122; *Z.* [2] 5, 198).—5. By reducing di-bromo-nitro-benzene (Wurster, *B.* 6, 1491).

Properties.—Needles or long plates.

Salts.—B'HCl.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$.

Acetyl derivative $C_6H_3Br_2NHAc$. [146°].

Benzoyl derivative $C_6H_3Br_2NBz_2$ [1:3:4]? [134°]. From benzanilide and Br (Hübner, *B.* 10, 1710).

s-**di-bromo-aniline** $C_6H_3Br_2(NH_2)$ [1:3:5]. [57°]. From *p*-nitro acetanilide, by successive conversion into nitro-aniline, di-bromo-nitro-aniline, and di-bromo-nitro-benzene, and reduction of the product (Körner, *G.* 4, 368; Langer, *A.* 215, 116). Needles.

Di-bromo-aniline $C_6H_3Br_2(NH_2)$ [1:2:4]. [80°]. From the corresponding di-bromo-nitro-benzene [58°] (Körner, *G.* 4, 370).

Di-bromo-aniline $C_6H_3Br_2(NH_2)$ [1:4:3]. [52°]. From the corresponding nitro- compound [85°] (Riche a. Bérard, *C. R.* 59, 141; Meyer a. Stuber, *A.* 165, 180).

Tri-bromo-aniline $C_6H_2Br_3(NH_2)$ [1:3:5:6]. [119°]. (300°).

by the action of bromine on aniline or on an aqueous solution of a salt of aniline (Fritzsche, *A.* 44, 291; *J. pr.* 28, 204; Hofmann, *A.* 53, 50).—2. By the action of Br on *o*- or *p*-bromo-aniline (Körner, *G.* 4, 305).—3. By reduction of tri-bromo-nitro-benzene (K.). 4. Together with aniline and di-bromo-aniline by the dry distillation of *p*-bromo-aniline or by heating it with HClAq at 160° (Buchner, *B.* 8, 361).

Preparation.—Bromine (500 g.) is gradually added to aniline (100 g.); as soon as a solid mass is formed glacial acetic acid is added and the addition of bromine continued until the mass has a red colour. The product is washed with dilute alcohol and water and crystallised from alcohol (H. Silberstein, *J. pr.* [2] 27, 101). Yield 80 per cent.

Properties.—Long colourless needles.

Reactions.—1. N_2O_3 passed into tri-bromo-aniline half dissolved, half suspended in alcohol, gives a yellow pp. of tribromo-diazo-benzene nitrate.—2. Converted by *diazo-reactions* into *s*-tri-bromo-benzene and into *u*-tetra-bromo-benzene.—3. Conc. HNO_3 gives di-bromo-di-nitro-methane, tetra-bromo quinone, *u*-tetra-bromo-benzene, picric acid, and oxalic acid (Losanitsch, *B.* 15, 472).

Salts. The salts are very unstable, and cannot be formed in aqueous solution. B'HBr: small white needles [190°], insol. ether and benzene; decomposed by water.—B'HCl: small white needles (Gattermann, *B.* 16, 635).

Acetyl derivative $C_6H_2Br_3NHAc$. [232°] (Remmers, *B.* 7, 349).

Diacetyl derivative $C_6H_2Br_3NAc_2$. [123°].

Tri-bromo-aniline $C_6H_2Br_3(NH_2)$ [1:2:3:5]. [above 130°]. From tri-bromo-nitro-benzene [112°] (Körner, *G.* 4, 328). Its salts are not decomposed by water.

Tetra-bromo-aniline $C_6HBr_4(NH_2)$ [1:2:3:5:6]. [115°]. Formed by brominating *m*-bromo-aniline, or (1, 4, 3)-di-bromo aniline (Körner, *G.* 4, 328; Wurster a. Nölting, *B.* 7, 1564). Is a by-product in the action of bromine on nitro-benzene in presence of Fe_2Br_6 (Scheufelen, *A.* 231, 161). Needles. Converted by the diazo-reaction into *u*-tetra-bromo-benzene.

Penta-bromo-aniline $C_6Br_5NH_2$. [222°]. Obtained by brominating (1, 3, 5)-di-bromo-aniline (Körner, *G.* 4, 368). Large needles (from alcohol mixed with toluene).

BROMO-ANILINE SULPHONIC ACID *v.* Bromo-amido-benzene sulphonic acid.

BROMO-ANISIC ACID *v. Methyl derivative of* Bromo-oxy-benzoic acid.

BROMO-ANISIDINE *v.* *Methyl*-Bromo-amido-phenol.

BROMO-ANTHRACENE $C_{14}H_9Br$. [100°]. Obtained by warming anthracene dibromide. Needles. Forms a red picric acid compound.

(*A.* 1,2)-**Di-bromo-anthracene** $C_{14}H_8Br_2$. [221°]. From Br and anthracene in CS_2 (Graebe a. Liebermann, *A. Suppl.* 7, 275). From triphenyl-methane in CS_2 and bromine in sunlight (tri-phenyl-methyl bromide being also formed) (Allen a. Kölliker, *A.* 227, 109; 228, 251). Golden needles (from toluene); may be sublimed. V. sl. sol. alcohol and ether. Alcoholic KOH at 100° forms anthracene. Dilute HNO_3 gives anthra-quinone. The compound with picric acid is re... Combines with Br forming $C_{14}H_8Br_6$ [170°-180°] decomposed at 180° into tri-bromo-anthracene, HBr, and Br.

Di-bromo-anthracene $C_{14}H_8Br_2$ [*B.* 1:2]? [192°]. From di-bromo-anthraquinone, HI, and P at 150° (Miller, *A.* 182, 367). Golden tables (from alcohol). Oxidises to di-bromo-anthraquinone.

Tri-bromo-anthracene $C_{14}H_7Br_3$. (*A.* 1, 2. *B.*) [169°]. Formed by heating (*A.* 1, 2)-di-bromo-anthracene tetrabromide (G. a. L.). Yellow needles (from benzene). Oxidised by HNO_3 to bromo-anthraquinone (Claus a. Hertel, *B.* 14, 979).—Bromide: $C_{14}H_7Br_7$.

Tetra-bromo-anthracene

$C_{14}H_6Br_4$ (*A.* 1, 2, *B.* 1, 2)? [254°]. From di-bromo-anthracene tetrabromide and alcoholic KOH (Anderson, *A.* 122, 304; G. a. L.). Yellow needles (from xylene). Gives di-bromo-anthraquinone on oxidation.—Bromide: $C_{14}H_6Br_8$ [212°] (Hammerschlag, *B.* 10, 1212).

Penta-bromo-anthracene $C_{14}H_5Br_5$. [212°]. Formed by heating tetra-bromo-anthracene tetrabromide at 230° (H.). Yellow powder. Oxidises to tetra-bromo-anthraquinone.

Hexa-bromo-anthracene $C_{14}H_4Br_6$. [310°–320°]. Prepared by the action of Br in presence of I on di-bromo-anthracene (Diehl, *B.* 11, 178). Oxidised by $K_2Cr_2O_7$ and H_2SO_4 to tetra-bromo-anthraquinone [c. 300°].

Hexa-bromo-anthracene $C_{14}H_4Br_6$. [above 370°]. From $C_{14}H_6Br_8$ and alcoholic NaOH (H.). Silky yellow needles (from kerosene). Oxidation gives tetra-bromo-anthraquinone [above 370°].

Hepta-bromo-anthracene $C_{14}H_3Br_7$. [above 350°]. Prepared by the prolonged action of Br at 200° in presence of I on di-bromo-anthracene (D.). Yellow needles. Insol. alcohol and ether.

Octo-bromo-anthracene $C_{14}H_2Br_8$. Formed by very prolonged action of iodine bromide at 360° on hepta-bromo-anthracene (D.). Needles. Insol. most ordinary solvents, sl. sol. nitro-benzene and aniline.

(*A.* 1) - **BROMO - ANTHRACENE** - (*A.* 2) - **CARBOXYLIC ACID** $C_6H_4{<}\begin{matrix}C(CO_2H)\\CBr\end{matrix}{>}C_6H_4$. [266°]. Formed by the action of bromine upon anthracene-(*A.*)-carboxylic acid in acetic acid. Long glistening yellow needles. Sublimable. Sol. alcohol, ether, and acetic acid, v. sl. sol. benzene and water. Its solutions have a blue fluorescence. Evolves CO_2 at its melting-point leaving bromo-anthracene.

Salts.—AgA': yellow microscopic prisms. —KA': long very slender yellow needles.— BaA'_2: yellowish needles (Behla, *B.* 20, 704).

DI-BROMO-ANTHRACENE DISULPHONIC ACID $C_{14}H_6Br_2(SO_3H)_2$. From di-bromo-anthracene and fuming H_2SO_4 (Perkin, *C. J.* 24, 19). Oxidises to anthraquinone disulphonic acid.

Salts.—Na_2A''.—BaA''.

BROMO-ANTHRANOL $C_{14}H_9OBr$ *i.e.*

$$C_6H_4{<}\begin{matrix}C(OH)\\|\\CBr\end{matrix}{>}C_6H_4 \quad\text{or}\quad C_6H_4{<}\begin{matrix}CO\\CBrH\end{matrix}{>}C_6H_4$$

[148°-151°]. Formed by the action of (1 mol. of) bromine upon anthranol (1 mol.) dissolved in CS_2. Yellowish crystals. Insol. boiling aqueous, but converted by cold alcoholic KOH into an orange K salt (Goldmann, *B.* 20, 2437).

Di-bromo-anthranol $C_{14}H_8OBr_2$ *i.e.* $C_6H_4<^{CO}_{CBr_2}>C_6H_4$. *Anthraquinone-bromide.* [157°]. Formed by the action of (rather more than 2 mol. of) bromine upon anthranol (1 mol.) dissolved in CS_2. Large rhombic crystals. Insol. aqueous alkalis. By boiling with acetic acid it is readily converted into anthraquinone.

(*B.* 1)-**BROMO-ANTHRAQUINONE** $C_{14}H_7BrO_2$. [188°]. Yellow needles. Sublimable. Prepared by heating *o*-bromo-benzoyl-benzoic acid $C_6H_4Br.CO.C_6H_4.CO_2H$ with H_2SO_4 to 180°. On fusion with KOH it gives *erythro*-oxy-anthraquinone (Pechmann, *B.* 12, 2127).

(*B.* 2) - **Bromo - anthraquinone** $C_{14}H_7BrO_2$. [187°]. Formed by oxidation of tri-bromo-anthracene with CrO_3 and HOAc (Graebe a. Liebermann, *A. Suppl.* 7, 290). Yellow needles; may be sublimed; sl. sol. alcohol, m. sol. hot benzene. Converted by potash-fusion into alizarin.

Di-bromo-anthraquinone $C_{14}H_6O_2Br_2$. [265°]. *Formation.* — 1. By brominating anthraquinone (Graebe a. Liebermann, *A. Suppl.* 7, 289; Diehl, *B.* 11, 181). - 2. By oxidation of tetra-bromo-anthracene or di-chloro-di-bromo-anthracene with CrO_3 (G. a. L.; Hammerschlag, *B.* 19, 1107).

Properties.—Boils with slight decomposition, sl. sol. boiling alcohol, m. sol. glacial HOAc. Potash-fusion at 250° gives alizarin. According to Perkin (*C. J.* 37, 554; *priv. com.*) the di-bromo-anthraquinone formed by the first method melts at 245° (or 250° cor.) and differs from that formed by the second method, which melts at 275° (or 281·5° cor.) by giving, on potash-fusion, not only alizarin but also flavopurpurin and anthrapurpurin (tri-oxy-anthraquinone).

Tri-bromo-anthraquinone $C_{14}H_5Br_3O_2$. [186°]. Prepared by the action of Br in presence of I upon anthraquinone or di-bromo-anthraquinone at 260° (Diehl, *B.* 11, 182). Yellow needles; insol. alcohol.

Tri - bromo - anthraquinone $C_{14}H_5Br_3O_2$. [365°]. From penta-bromo-anthracene, CrO_3, and HOAc (Hammerschlag, *B.* 10, 1213). Flat needles (by sublimation).

Tetra - bromo - anthraquinone $C_{14}H_4Br_4O_2$. [295°-300°]. Formed by oxidising hexa-bromo-anthracene [320°] or by brominating tri-bromo-anthraquinone [186°] in presence of I (D.). Yellow needles.

Tetra - bromo - anthraquinone $C_{14}H_4Br_4O_2$. [above 370°]. Formed by oxidising hexa-bromo-anthracene [above 370°] (H.). Yellow needles.

Penta - bromo - anthraquinone $C_{14}H_3Br_5O_2$. Formed by oxidation of hepta-bromo-anthracene (D.). Sublimes with difficulty without melting; sl. sol. boiling toluene.

DI - BROMO - DIANTHRYL $C_{28}H_{16}Br_2$. [far above 300°]. Yellow prisms (from toluene). Formed by bromination of dianthryl dissolved in CS_2 (Liebermann a. Gimbel, *B.* 20, 1855).

DI - BROMO - APOPHYLLENIC ACID $C_8H_6BrNO_4$ *i.e.* $C_5NH_2Br(CO_2H)(CO_2Me)$ or $C_5NH_2MeBr(CO_2H)<^{CO}_{O}>$. *Methyl-ether of bromo-pyridine dicarboxylic acid?* From bromo-tarconine (a derivative of narcotine) and Br (v. Gerichten, *A.* 210, 91). Hard prisms (containing 2aq); sol. hot water. Its solutions give no pps. with salts of Pb, Ag, or Cu. Heated with conc. HCl it forms CO_2, MeCl, and a bromo-pyridine carboxylic acid (?) [199°].

Salt.—BaA'_2 3aq.

DI - BROMO - APOPHYLLIN $C_{16}H_{10}Br_4N_2O_4$. [229°]. From bromo-tarconine or bromo-apophyllenic acid and bromine-water (v. Gerichten, *A.* 210, 94). Six-sided tables (containing 4aq); sol. water, insol. ether. Alkalis form a deep-red solution. HCl at 150° gives CO_2, MeCl, di-bromo-pyridine, and di-bromo-pyridine methylo-chloride.

Salts.—B″HCl.—B″2HCl.—$B''_2H_2PtCl_6$aq.—B″HBr.—B″2HBr.

DI - BROMO - ATROLACTIC ACID *v.* ββ-DI-BROMO-α-OXY-α-PHENYL-PROPIONIC ACID.

BROMO - ATROPIC ACID $C_9H_7BrO_2$ *i.e.* $Ph.C_2HBr.CO_2H$. *Exo-bromo-α-phenyl-acrylic acid.* [130°]. From the compound of atropic acid (1 mol.) with HBr (2 mols.) by boiling with water (Fittig a. Wurster, *A.* 195, 162). Slender needles (from water).

TETRA - BROMO - AURIN $C_{19}H_{10}Br_4O_3$. Formed by brominating aurin dissolved in HOAc (Dale a. Schorlemmer, *C. J.* 35, 152; *cf.* Zulkowsky, *M.* 3, 465). Bronzed crystals. Alkalis form violet solutions.

Salt.—$A''Ag_2$: dark violet insoluble pp.

Ethyl ether $A''Et_2$: [110°-115°]; microscopic reddish crystals; sol. alcohol, ether, and benzene (Ackermann, *B.* 17, 1626).

BROMO-AZO-BENZENE *v.* pp. 374, 379.

TETRA-BROMO-AZOPHENINE $C_{30}H_{20}Br_4N_4$. [243°]. Formed by heating *p*-nitroso-di-phenylamine with *p*-bromo-aniline and *p*-bromo aniline hydrochloride at 100°. Greatly resembles azophenine (O. Fischer a. Hepp, *B.* 20, 2481).

BROMO-AZO-TOLUENE *v.* p. 394.

DI-BROMO-AZOXY-BENZENE *v.* p. 427.

BROMO-AZOXY-TOLUENE *v.* p. 428.

BROMO - BARBITURIC ACID $C_4H_3BrN_2O_3$, *i.e.* $CHBr<^{CO.NH}_{CO.NH}>CO$. *Bromo-malonyl-urea. Ureide of bromo-malonic acid.* From di-bromo-barbituric acid by reduction with Na or Zn, or by evaporating with aqueous HCN (Baeyer, *A.* 130, 134). Small needles; sl. sol. cold water.

Salts.— NH_4A'. — ZnA'_2 8aq. — ZnA'_2 6aq (Mulder, *B.* 12, 2309).

Di-bromo-barbituric acid $C_4H_2Br_2N_2O_3$. *Di-bromo-malonyl-urea.* Formed by the action of Br on barbituric, nitro-barbituric, nitroso-barbituric, and hydurilic acids (Baeyer, *A.* 127, 199; 130, 130).

Preparation.—From di-bromo-oxy-methyl-uracil and fuming HNO_3 (Behrend, *A.* 236, 62).

Properties.—Trimetric crystals. Sol. water, v. sol. hot alcohol and ether.

Reactions.—1. Boiling *water* forms alloxan and HBr.—2. HI reduces it to hydurilic and barbituric acids.—3. H_2S forms dialuric acid.—4. *Bromine water* forms CO_2 and tri-bromo-acetyl urea.—5. *Alkalis* form CO_2, tri-bromo-acetyl urea, and bromo-barbituric acid.—6. *Thio-urea* forms so-called thio-pseudo-uric acid $C_5N_4H_6O_3S$ (Trzcinski, *B.* 16, 1057).—7. *Potassium sulphocyanide* forms sulphocyano-barbituric acid $C_5N_3H_3SO_3$ (T.).

Di-bromo-di-barbituric acid $C_8H_4Br_2N_4O_6$ aq. Prisms (Baeyer, *A.* 130, 145; *cf.* p. 440). — $C_8H_4Br_2N_4O_6HBr$. Prisms, v. sl. sol. water.

DI-BROMO-BEHENIC ACID $C_{22}H_{42}Br_2O_2$. [43°]. From erucic acid $C_{22}H_{42}O_2$ and bromine (Haussknecht, *A.* 143, 40; Otto, *A.* 135, 226). Nodules. Converted by alcoholic KOH to bromo-erucic acid, $C_{22}H_{41}BrO_2$ and behenolic acid $C_{22}H_{40}O_2$. Moist Ag_2O forms oxy-erucic acid and di-oxy-behenic acid. Sodium amalgam forms erucic acid. Salts.—BaA'_2.—PbA'_2.

Di-bromo-behenic acid $C_{22}H_{42}Br_2O_2$. [54°]. From brassic acid and bromine (H.). Reduced by sodium-amalgam to brassic acid. Alcoholic KOH at 220° gives behenolic acid.

Tri-bromo-behenic acid $C_{22}H_{41}Br_3O_2$. [32°]. From bromo-erucic acid and bromine (H.).

Tetra-bromo-behenic acid $C_{22}H_{40}Br_4O_2$. [78°]. From behenolic acid and bromine (H.). Laminæ (from alcohol).

BROMO-BENZALDEHYDE *v.* BROMO-BENZOIC ALDEHYDE.

BROMO-BENZAMIDE *v. Amide of* BROMO-BENZOIC ACID.

BROMO-BENZANILIDE *v. Anilide of* BROMO-BENZOIC ACID.

BROMO-BENZENE C_6H_5Br. *Phenyl bromide.* Mol. w. 157. (156°). S.G. $\frac{20}{4}$ 1·4911. μ_β 1·5736. R_∞ 55·81 (Brühl). S.V. 119·9 (Schiff, *B.* 19, 564). *Vapour pressure*: Ramsay a. Young, *C. J.* 47, 646.

Formation.—1. From bromine and benzene, either boiling or in sunlight (Couper, *A. Ch.* [3] 52, 309; Schramm, *B.* 18, 606). The reaction is promoted by the presence of I (Ador a. Rilliet, *B.* 8, 1287) or Al_2Cl_6 (Greene, *C. R.* 90, 40; Leroy, *Bl.* [2] 48, 210).—2. Formed by running a solution of $NaNO_2$ into a hot solution of Cu_2Br_2 and aniline in dilute H_2SO_4 (Sandmeyer, *B.* 17, 2652).—3. By heating diazobenzene with a large excess of strong HBr; the yield is 32 p.c. of the theoretical (Gasiorowski a. Wayss, *B.* 18, 1938). 4. From phenol and bromide of phosphorus (Riche, *A.* 121, 357).

Properties.—Oil; not attacked by KOH, KCy, or AgOAc.

Reactions.—1. Boiling with Al_2Cl_6 produces benzene and di-bromo-benzenes (Dumreicher, *B.* 15, 1867).—2. Converted in the animal system into *p*-bromo-phenyl-mercapturic acid $C_{11}H_{12}BrNSO_3$, *p*-bromo-phenol, bromo-pyrocatechin, and bromo-hydroquinone (Baumann a. Preusse, *H.* 3, 156; Jaffé, *B.* 12, 1092).—3. Converted by conc. H_2SO_4 into di-bromo-benzene sulphonic acid and bromo-benzene di-sulphonic acid (Herzig, *M.* 2, 192).—4. $ClSO_3H$ forms $C_6H_4Br(SO_3H)$ [1:4] and $C_6H_4Br.SO_2.C_6H_4Br$ (Beckurts a. Otto, *B.* 11, 2061).—5. Heating with MeONa gives C_6H_5OMe and phenol (Blau, *M.* 7, 621). According to Mittica (*B.* 17, 2634) there is a second bromo-benzene [c. 62°].

o-**Di-bromo-benzene** $C_6H_4Br_2$ [1:2]. [−1°]. (224°). S.G. $\frac{0}{}$ 2·003. Formed in small quantity in preparing *p*-di-bromo-benzene from benzene and Br (Riese, *B.* 2, 61; *A.* 164, 176). Formed also from *o*-nitraniline *viâ* *o*-bromo-nitro-benzene (Körner, *G.* 4, 333). HNO_3 forms chiefly di-bromo-nitro-benzene [58°].

m-**Di-bromo-benzene** $C_6H_4Br_2$ [1:3]. (219°). S.G. $\frac{18·6}{4}$ 1·955.

Formation.—1. From (1,3,4)-di-bromo-aniline (Meyer a. Stüber, *A.* 165, 169).—2. From *s*-di-bromo-aniline.—3. From *m*-di-nitro-benzene *viâ* *m*-nitro-aniline, *m*-bromo-nitro-benzene, and *m*-bromo-aniline (K.).—4. Together with the *p*- isomeride by the action of Br on benzene in presence of Al_2Cl_6 (Leroy, *Bl.* [2] 48, 211).

Properties.—Has not been solidified. Yields with HNO_3 two nitro-derivatives [62°] and [83°]. Sodium acting on an ethereal solution forms diphenyl, $C_{48}H_{32}Br_2$ [220°] and $C_{78}H_{52}Br_2$ [250°], (Goldschmiedt, *M.* 7, 45).

p-**Di-bromo-benzene** $C_6H_4Br_2$ [1:4]. [89°]. (219°). S.V.S. 127·8 (Schiff).

Formation.—1. By bromination of benzene or bromo-benzene (Couper, *A. Ch.* [3] 52, 309; Riche a. Bérard, *A.* 133, 51; Riese, *A.* 164, 162; Jannasch, *B.* 10, 1355).—2. From *p*-diazo-bromo-benzene perbromide by heating with alcohol (Griess, *C. J.* 20, 66).—3. From *p*-bromo-phenol and PBr_5 (A. Mayer, *A.* 137, 219).—4. From benzene, Br, and Fe_2Cl_6 (Scheufelen, *A.* 231, 188).

Preparation.—1. By treating benzene with Br and a little I.—2. Bromine (960 g.) is added slowly to benzene (240 g.) and Al_2Cl_6 (30 g.). On adding water in excess, the product deposited consists of crystals of the para- compound, with an oil, consisting chiefly of the meta- compound. This oil, however, contains some para-di-bromo-benzene in solution. To separate this, the oil is treated with fuming H_2SO_4. The meta- derivative is easily sulphonated in this way, but the para- is not affected. On adding a large excess of water, the solid $C_6H_4Br_2$ [1:4] is ppd., and the clear solution of the meta-sulphonate distilled with steam gives $C_6H_4Br_2$ [1:3] (Leroy, *Bl.* [2] 48, 211).

Properties.—Prisms or plates, isomorphous with *p*-di-chloro-benzene (Friedel, *Bl.* [2] 11, 38). Sublimable. Sl. sol. alcohol.

Reactions.—1. Heated for 30 minutes with Al_2Cl_6 (⅛ part) gives C_6H_5Br, $C_6H_4Br_2$ [1:3], and two tribromobenzenes, $C_6H_3Br_3$ [1:2:4] and [1:3:5] (L.).—2. HNO_3 forms a nitro-derivative [85°].—3. In ethereal solution *sodium* forms diphenyl, di-phenyl-benzene, and $C_{48}H_{32}Br_2$ [265°] and $C_{78}H_{52}Br_2$ [300°] (Riese, *A.* 164, 164; Goldschmiedt, *M.* 7, 42).—4. MeI and Na form *p*-xylene.—5. NaOEt at 190° gives C_6H_4BrOEt, bromo-benzene, and benzene (Balbiano, *G.* 11, 401).—6. NaOMe forms C_6H_4BrOMe, $C_6H_4(OMe)_2$ and $C_6H_4(OMe)(OH)$ (Blau, *M.* 7, 621).—7. Converted by conc. H_2SO_4 into tetra- and hexa-bromo-benzene (Herzig, *M.* 2, 192).

v-**Tri-bromo-benzene** $C_6H_3Br_3$ [1:2:3]. Mol. w. 315. [87°]. From (1,3,5,2)-di-bromo-nitro-aniline *viâ* tri-bromo-nitro-benzene, and tri-bromo-aniline (Körner, *G.* 4, 401). Tables (from alcohol); may be sublimed.

s-**Tri-bromo-benzene** $C_6H_3Br_3$ [1:3:5]. [119°]. (278°). *Formation.*—1. From ordinary tri-bromo-aniline (Stüber, *B.* 4, 956; *A.* 165, 173; Reinke, *A.* 186, 271; Bässmann, *A.* 191, 206; Silberstein, *J. pr.* [2] 27, 104).—2. From (1,3,5)-di-bromo-aniline (K.).—3. In small quantity by the action of light on bromo-acetylene (Sabanejeff, *J. R.* 17, 176).

Properties.—Needles (from alcohol); sl. sol. alcohol. Boiling conc. H_2SO_4 forms hexa-bromo-benzene (Herzig, *M.* 2, 197). NaOMe

forms $C_6H_2Br_3(OH)$ and $C_6H_2Br_3OMe$ [77°] (Blau, *M.* 7, 621).

u-Tri-bromo-benzene $C_6H_3Br_3$ [1:2:4]. [44°]. (275°). *Formation.*—1. From hexa-bromo-benzene and alcoholic KOH (Mitscherlich, *P.* 35, 374; Lassaigne, *Rev. Scient.* 5, 360).—2. From (1,3,4)-di-bromo-phenol and PBr_5 (Mayer, *A.* 137, 224).—3. From (1,3,4)-di-bromo-aniline (Griess, *Tr.* 154, 667).—4. From *o*-, *m*-, and *p*-, di-bromo-benzene by nitration, reduction, and diazotisation (K.).—5. Got from each of the dibromobenzenes by heating with water and bromine at 250° (Wroblewsky, *A.* 192, 220).—6. From benzene, bromine, and Fe_2Cl_6 (Scheufelen, *A.* 231, 188).—7. As a by-product, in the preparation of $C_6H_4Br_2$ by the action of Br_2 upon C_6H_6 in presence of Al_2Cl_6 (Leroy, *Bl.* [2] 48, 213). *Properties.*—Needles; sl. sol. alcohol.

s-Tetra-bromo-benzene $C_6H_2Br_4$ [1:2:4:5]. Mol. w. 394. [175°]. *Formation.*—1. From *p*-di-bromo-benzene and Br at 150° (Riche a. Bérard, *A.* 133, 51).—2. From *u*-tri-bromo-benzene and Br. 3. From nitro-benzene and Br at 250° (Meyer, *B.* 15, 46).—4. From benzene (30 g.), Fe_2Cl_6 (5 g.), and bromine (240 g.); the mixture must be cooled (Scheufelen, *A.* 231, 187). *Properties.*—Long needles (from alcohol).

u-Tetra-bromo-benzene $C_6H_2Br_4$ [1:2:3:5]. [98·5°]. (329°). *Formation.*—1. From (1,3,5,2)-tri-bromo-phenol and PBr_5 (Körner, *A.* 137, 218; Mayer, *A.* 137, 227).—2. From (1,3,5,2)-tri-bromo-aniline (Wurster a. Nölting, *B.* 7, 1564; V. v. Richter, *B.* 8, 1428; Silberstein, *J. pr.* [2] 27, 118).—3. From $C_6HBr_4SO_3H$ by heating with HCl (Bässmann, *A.* 191, 224).—4. One of the products obtained by heating tri-bromo-diazo-benzene nitrate with benzene (Silberstein, *J. pr.* [2] 27, 110). *Properties.*—Long needles, v. sl. sol. alcohol. HNO_3 (S.G. 1·50) gives a nitro-derivative [96°]; fuming HNO_3 (S.G. 1·54) gives a di-nitro-derivative [228°].

Tetra-bromo-benzene $C_6H_2Br_4$. [160°]. From *p*-nitro-benzoic acid and Br at 280° (Halberstadt, *B.* 14, 911). Needles (from alcohol).

Tetra-bromo-benzene $C_6H_2Br_4$. [138°]. From *p*-di-bromo-benzene and boiling conc. H_2SO_4 (Herzig, *M.* 2, 195). One, if not both, of the two last-mentioned bodies is, doubtless, a mixture.

Penta-bromo-benzene C_6HBr_5. Mol. w. 473. [260°]. *Formation.*—1. From Br and nitro-benzene or di-nitro-benzene at 250° (Kekulé, *A.* 137, 172).—2. From *s*-tri-bromo-benzene and fuming H_2SO_4 at 100° (Bässmann, *A.* 191, 208).—3. From alizarin and BrI at 250° (Diehl, *B.* 11, 191). *Properties.*—Silky needles; v. sl. sol. alcohol, sol. benzene.

Hexa-bromo-benzene C_6Br_6. *Per-bromo-benzene.* [above 315°]. *Formation.*—1. By the action of Br containing I upon benzene, toluene, or benzene-azo-benzene at 250°–400° (Gessner, *B.* 9, 1505).—2. From tetra-bromo-quinone and PBr_5 at 280° (Ruoff, *B.* 10, 403).—3. From *p*-di-bromo-benzene (or tri-bromo-benzene) and conc. H_2SO_4 (Herzig, *M.* 2, 192).—4. By heating at 360° per-bromo-methane, per-bromo-ethane, per-bromo-butane, per-bromo-pentane, or per-bromo-hexane (Merz a. Weith, *B.* 11, 2235).—5. By heating benzene with bromine and Al_2Br_6.—6. By heating pentabromo-phenol with PBr_5 at 260° (Merz a. Weith, *B.* 16, 2890).—7. From bromine (800 g.), Fe_2Cl_6 and benzene (17 g.) in the cold. Good yield (110 g. instead of 119 g.) (Scheufelen, *A.* 231, 189). *Properties.*—Long needles (from toluene). V. sl. sol. alcohol and toluene.

BROMO-BENZENE *o*-SULPHONIC ACID $C_6H_4Br.SO_3H$ [1:2]. From *o*-amido-benzene sulphonic acid (Berndsen a. Limpricht, *A.* 177, 101; Bahlmann, *A.* 181, 203; 186, 315). Long deliquescent needles; v. e. sol. alcohol.—NH_4A'.—KA'aq.—BaA'_2 aq.—BaA'_2 2aq.—CaA'_2 2aq.—PbA'_2 3aq.—AgA'.

Chloride $C_6H_4Br.SO_2Cl$ [51°].

Amide $C_6H_4Br.SO_2NH_2$ [186°].

Bromo-benzene *m*-sulphonic acid $C_6H_4Br.SO_3H$ [1:3]. From amido-benzene *m*-sulphonic acid (Berndsen, *A.* 177, 92). Formed also by brominating benzene sulphonic acid or its silver salt (Ross Garrick, *Z.* [2] 5, 549; Genz, *B.* 2, 405; Nölting, *B.* 8, 819; Thomas, *A.* 186, 133). Very deliquescent.—KA'aq. S. (of KA') 4·4 at 0°.—PbA'_2 2aq.—PbA'_2 3aq.—S. (of PbA'_2) 5·78 at 7°.—BaA'_2 2aq. S. (of BaA'_2) 3·5 at 14°. CaA'_2.—AgA'.

Chloride $C_6H_4Br.SO_2Cl$. Oil.

Amide $C_6H_4Br.SO_2NH_2$. [154°].

Bromo-benzene-*p*-sulphonic acid $C_6H_4Br.SO_3H$ [1:4] [88°]. Deliquescent needles. *Formation.*—1. By sulphonating bromo-benzene with H_2SO_4, $ClSO_3H$, or SO_3 (Couper, *C. R.* 45, 230; Ross Garrick, *Z.* [2] 5, 549; Armstrong, *Z.* [2] 7, 321; Nölting, *B.* 8, 594).—2. From *p*-amido-benzene sulphonic acid (Meyer, *A.* 156, 291; Berndsen, *A.* 177, 92).

Reactions.—The K salt distilled with K_4FeCy_6 gives terephthalonitrile.

Salts.—(Goslich, *B.* 8, 352; *A.* 180, 93).—NH_4A'. KA'. CaA'_2 2aq.—BaA'_2.—PbA'_2 2aq.—PbA'_2.—ZnA'_2 6aq.—CuA'_2 6aq. AgA'.

Chloride $C_6H_4Br.SO_2Cl$. [75°].

Amide [164°] (Bässmann, *A.* 191, 247).

Acetyl-amide $C_6H_4Br.SO_2NHAc$ [199°].

Anilide $C_6H_4Br.SO_2NHPh$ [119°].

Bromo-benzene di-sulphonic acid $C_6H_3Br(SO_3H)_2$ [1:3:4?]. From the corresponding amido-benzene disulphonic acid (Zander, *A.* 198, 28). Deliquescent needles.—BaA'' 3aq.—PbA''aq.

Chloride $C_6H_3Br(SO_2Cl)_2$ [101°].

Amide $C_6H_3Br(SO_2NH_2)_2$ [210°].

Bromo-benzene di-sulphonic acid $C_6H_3Br(SO_3H)_2$ [1:2:4]. *Formation.*—1. From the corresponding amido-benzene disulphonic acid (Zander, *A.* 198, 10).—2. From bromo-benzene *p*-sulphonic acid and SO_3 at 210° (Nölting, *B.* 7, 1311). *Properties.*—Slender deliquescent needles. K_2A''aq.—BaA'' 4aq. S. (of BaA'') 6 at 22°.—Ag_2A''

Chloride $C_6H_3Br(SO_2Cl)_2$ [103°].

Amide $C_6H_3Br(SO_2NH_2)_2$ [239°].

Bromo-benzene di-sulphonic acid $C_6H_3Br(SO_3H)_2$ [1 or 4:5:3]. From the corresponding amido-benzene disulphonic acid (Heinzelman, *A.* 188, 177). Deliquescent needles.

Salts.—$(NH_4)_2A''$.—BaA'' 2½aq.—PbA'' 2½aq.

Chloride $C_6H_3Br(SO_2Cl)_2$ [99°].

Amide $C_6H_3Br(SO_2NH_2)_2$ [245°].

***o*-Di-bromo-benzene sulphonic acid** $C_6H_3Br_2(SO_3H)$ [1:2:3]. From the corresponding di-amido-benzene sulphonic acid (Sachse, *A.* 188, 153). Deliquescent prisms.

Salts.—KA'.—BaA'₂ 3aq. S. (of BaA'₂) ·143 at 10°.—CaA'₂ 2aq.—PbA'₂ 3aq.

Chloride $C_6H_3Br_2.SO_2Cl$ [127°].

Amide $C_6H_3Br_2.SO_2NH_2$ [215°].

o-Di-bromo-benzene sulphonic acid $C_6H_3Br_2(SO_3H)$ [1:2:4]. [67°]. From silver bromo-benzene *m*- or *p*- sulphonate and bromine (Limpricht a. Goslich, *A.* 186, 145). From $C_6H_3Br(NH_2)SO_3H$ by diazo- reaction (Langfurth, *A.* 191, 179; Spiegelberg, *A.* 197, 263). The free acid crystallises with 3aq [68°].

Salts.— KA'. — NH_4A'. — BaA'_2 2aq. — BaA'_2 3aq. S. (of BaA'_2) ·3 at 11°.—CaA'_2.—PbA'_2 2aq. S. (of PbA'_2) ·26 at 7°.—AgA'.

Chloride $C_6H_3Br_2SO_2Cl$. Oil.

Amide $C_6H_3Br_2SO_2NH_2$ [175°].

m-Di-bromo-benzene sulphonic acid $C_6H_3Br_2(SO_3H)$ [1:3:5]. From dibrominated *o*- or *p*- amido-benzene sulphonic acid by the diazo-reaction (Limpricht, *B.* 8, 1066; *A.* 181, 201; Schmitt, *A.* 120, 158; Lenz, *A.* 181, 23). It is also a product of the action of conc. H_2SO_4 on bromo-benzene (Herzig, *M.* 2, 192). Crystalline.

Salts.—NH_4A'.—KA'.—BaA'_2 3½aq. S. (of BaA'_2) ·28 at 18°. — CaA'_2 3½aq. — PbA'_2 1½aq. S. (of PbA'_2) ·21 at 18°.

Chloride $C_6H_3Br_2SO_2Cl$. [57·5°].

Amide $C_6H_3Br_2SO_2NH_2$. [203°].

m-Di-bromo-benzene sulphonic acid $C_6H_3Br_2SO_3H$ [1:3:4]. [80° when hydrated]; [110° anhydrous]. From $C_6H_2Br_2(NH_2)SO_3H$ [1:3:4:6] by diazo- reaction (Langfurth, *A.* 191, 184; Bässmann, *A.* 191, 232). Slender deliquescent needles (containing aq). Sol. alcohol, insol. ether. With HBr at 180° gives H_2SO_4 and *m*-di-bromo-benzene.

Salts.—NH_4A'.—KA'.—BaA'_2 2½aq (L.).—BaA'_2 2aq (B.). S. (anhydrous) 2 at 10° (L.); 1 at 20° (B.).—CaA'_2 3aq. S. (anhydrous) 8·34 at 10°.—PbA'_2 3aq. S. (anhydrous) 1·43 at 8°.—AgA'.

Chloride $C_6H_3Br_2SO_2Cl$. [79°]. c

Amide $C_6H_3Br_2SO_2NH_2$. [190°] (anhydrous).

p-Di-bromo-benzene sulphonic acid $C_6H_3Br_2(SO_3H)$ [1:4:2]. [128°].

Formation.—1. By bromination of silver *o*- or *m*-bromo-benzene sulphonate (Bahlmann, *A.* 181, 206; Limpricht, *A.* 186, 139).—2. By sulphonation of *p*-di-bromo-benzene (Douglas Williams, *Z.* [2] 7, 302; Hübner a. Williams, *A.* 167, 117; Wölz, *A.* 168, 81).—3. From nitrated bromo-benzene *o*- or *m*-sulphonic acid (Thomas, *A.* 186, 129; B.).—4. From brominated amido-benzene o-sulphonic acid (B.). Prisms (containing 3aq). [98°]. Conc. HBr at 250° gives H_2SO_4 and *p*-di-bromo-benzene.

Salts.—(*cf.* Borns, *A.* 187, 350).—NH_4A'.—NaA' 1½aq.—KA' aq. S. (of KA') 5·79 at 21°.—AgA' 1½aq. AgA' 3aq. S. (of AgA') 1·69 at 10°.—BaA'_2. S. 1·01 at 16°.—BaA'_2 aq.—BaA'_2 2aq.—BaA'_2 5aq.—CaA'_2 4aq. S. (of CaA'_2) 5·90 at 22°.—CaA'_2 5aq.—CaA'_2 10aq.—PbA'_2 3aq. S. (of PbA'_2) 2·56 at 21°.—PbA'_2 4aq.—CuA'_2 14aq.

Chloride $C_6H_3Br_2(SO_2Cl)$: [72°].

Amide $C_6H_3Br_2(SO_2NH_2)$. [193°].

Anhydride $(C_6H_3Br_2SO_2)_2O$. Obtained by the action of fuming sulphuric acid upon *p*-di-bromo-benzene. Amorphous powder. Nearly insol. alcohol, ether, and benzene. By boiling alkalis it is converted into salts of the acid; very slowly attacked by boiling water. PCl_5 converts it into the chloride (Rosenberg, *B.* 19, 653).

m-Di-bromo-benzene di-sulphonic acid $C_6H_2Br_2(SO_3H)_2$. From $C_6H_2(NO_2)_2(SO_3H)_2$ (Limpricht, *B.* 8, 290). Deliquescent.

p-Di-bromo-benzene disulphonic acid $C_6H_2Br_2(SO_3H)_2$. Formed by sulphonating *p*-di-bromo-benzene (Borns, *A.* 187, 366). Small columns.—K_2A''.—BaA'' 4½aq.

Chloride $C_6H_2Br_2(SO_2Cl)_2$. [161°].

Amide $C_6H_2Br_2(SO_2NH_2)_2$. [210°].

Tri-bromo-benzene sulphonic acid $C_6H_2Br_3SO_3H$ [1:3:5:6]. [145°] (anhydrous). Formed by sulphonating *s*-tri-bromo-benzene (Reinke, *A.* 186, 271; Bässmann, *A.* 191, 206). Also from $C_6H(NH_2)Br_3SO_3H$ [1:2:4:6:3] by diazo-reaction (Langfurth, *A.* 191, 191). Six-sided tables (containing aq) [95°]. Water at 180° forms H_2SO_4 and *s*-tri-bromo-benzene.

Salts.—NH_4A' aq.—KA' 3aq.—KA' aq. S. (of KA') ·81 at 5·5 (B.).—BaA'_2 9aq.—BaA'_2 6aq.—BaA'_2 2aq. S. (of BaA'_2) ·41 at 5·5° (L.); ·22 at 7·5° (B.).—CaA'_2 8aq. S. (of CaA'_2) 1·95 at 7° (L.); 3·5 at 2·5° (B.).—CaA'_2 4aq.—CaA'_2 7aq.—PbA'_2 aq.—PbA'_2 9aq.—PbA'_2 2aq. S. (of PbA'_2) ·36 at 7° (B.).—AgA' aq.

Chloride. $C_6H_2Br_3SO_2Cl$. [65°].

Amide. $C_6H_2Br_3SO_2NH_2$. Decomposes above 220°.

Tri-bromo-benzene sulphonic acid $C_6H_2Br_3.SO_3H$ [1:2:4:5]. [140° anhydrous]. From (1, 2, 4, 5)- or (2, 4, 1, 5)-di-bromo-amido-benzene sulphonic acid by diazo-reaction (Langfurth, *A.* 191, 188; Reinke, *A.* 186, 288; Knuth, *A.* 186, 303; Spiegelberg, *A.* 197, 282). Needles (containing 3aq) [80°]. With HBr at 200° gives H_2SO_4 and $C_6H_3Br_3$ [1:2:4].

Salts.—NH_4A'aq.—KA'aq. S. (of KA') 1·03 at 20° (B.); ·77 at 22° (S.).—BaA'_2 3aq. S. ·122 at 12°.—BaA'_2 2aq.—BaA'_2 6aq.—CaA'_2 6aq.—PbA'_2 4aq.—AgA'.

Chloride.—$C_6H_2Br_3SO_2Cl$ [86·5°].

Amide.—$C_6H_2Br_3SO_2NH_2$ [c. 225°].

Anhydride $(C_6H_2Br_3SO_2)_2O$. Obtained by the action of fuming sulphuric acid upon tri-bromo-benzene (1:2:4). Amorphous powder. Almost insol. alcohol, ether, and benzene. By boiling aqueous alkalis it is converted into salts of the acid; only very slowly attacked by boiling water. PCl_5 converts it into the chloride (*v. supra*) (Rosenberg, *B.* 19, 654).

Tri-bromo-benzene sulphonic acid $C_6H_2Br_3SO_3H$ [1:2:3:5]. From di-brominated amido-benzene *p*-sulphonic acid (Lenz, *B.* 8, 1067; *A.* 181, 29). — NH_4A'. — KA'.—CaA'_2 2½aq. S. ·39 at 20°.—BaA'_2 3aq. S. (of BaA'_2) ·021 at 18°.—PbA'_2 3½aq. S. ·056 at 21°.

Chloride $C_6H_2Br_3SO_2Cl$. [127°].

Amide $C_6H_2Br_3SO_2NH_2$ [210°].

Tri-bromo-benzene sulphonic acid $C_6H_2Br_3SO_3H$ [1?:2:3:5]. From silver (1, 2, 4)-di-bromo-benzene sulphonate and Br (Goslich, *A.* 186, 154). Is perhaps identical with the preceding.—BaA'_2 3½aq.

Chloride [121°]. *Amide* [152°].

Tri-bromo-benzene sulphonic acid $C_6H_2Br_3SO_3H$ [1:3:4:5]. From nitrated (1, 3, 5)-di-bromo-benzene sulphonic acid (Lenz, *A.* 181, 39).—KA'aq.—BaA'_2aq.

Chloride $C_6H_2Br_3SO_2Cl$. [86°].

Amide $C_6H_2Br_3SO_2NH_2$. Blackens at 225°.

Tri-bromo-benzene sulphonic acid $C_6H_2Br_3SO_3H$. Possibly identical with the preceding. From nitrated (1, 4, 2)-di-bromo-benzene sulphonic acid (Borns, *A.* 187, 364).—KA' 3½aq.—$BaA'_2$2aq.

Amide [above 220°].

Tri-bromo-benzene sulphonic acid $C_6H_2Br_3SO_3H$. From silver bromo-benzene *o*-sulphonate and Br (Bahlmann, *A.* 181, 207).

Chloride $C_6H_2Br_3SO_2Cl$. [56°].

Amide $C_6H_2Br_3SO_2NH_2$. [202°].

Tri-bromo-benzene sulphonic acid $C_6H_2Br_3SO_3H$. Formed at the same time as the preceding (B.).

Chloride $C_6H_2Br_3SO_2Cl$. [72°].

Amide $C_6H_2Br_3SO_2NH_2$. [187°].

Nine tri-bromo-benzene sulphonic acids are here described, but only six are indicated by theory.

Tri-bromo-benzene di-sulphonic acid $C_6HBr_3(SO_3H)_2$. From benzene *m*-di-sulphonic acid by nitration, reduction, bromination to $C_6HBr_2(NH_2)(SO_3H)_2$ and diazotisation (Heinzelmann, *A.* 188, 183).—Salt: K_2A''.

Tetra-bromo-benzene-sulphonic acid $C_6HBr_4SO_3H$ 5aq [1:2:3:5.6].

Formation. — 1. From $C_6HBr_3(NH_2)SO_3H$ [1:3:5:4:6] by diazo- reaction (Beckurts, *A.* 181, 216; Langfurth, *A.* 191, 199; Knuth, *A.* 186, 229; Reincke, *A.* 186, 282).—2. From $C_6H_2Br_4$ and H_2SO_4 (Bässmann, *A.* 191, 223). Needles. Not hygroscopic but v. sol. alcohol and water.

Reaction.—With conc. HBr at 150° gives H_2SO_4 and (1,2,3,5)-tetra-bromo-benzene [98·5°].

Salts.—KA'. S. ·63 at 6°.—BaA'_2. S. ·37 at 12° (L.); ·16 at 15° (Bä.).—BaA'_2 1½aq.—$CaA'_2$8aq. S. (of CaA'_2) ·54 at 3°; ·66 at 19° (Bä.).—NH_4A'.—PbA'_2PbO 3aq.—PbA'_2 1½aq. S. (of PbA'_2) ·89 at 11° (Bä.).—PbA'_2 4aq.

Chloride $C_6HBr_4SO_2Cl$. [96°].

Amide $C_6HBr_4SO_2NH_2$. Minute needles. Not melted at 300°.

Tetra-bromo-benzene sulphonic acid $C_6HBr_4(SO_3H)$ [1:2:3:4:5]. [169°]. From (1,2,3,5)-tri-bromo-benzene sulphonic acid by nitration, reduction, and diazotisation (Lenz, *A.* 181, 23). Also in the same way from (1,2,4,5)-tri-bromo-benzene sulphonic acid (Spiegelberg, *A.* 197, 292). Laminæ (containing 2aq).

Salts.—KA'aq. S. (of KA') ·194 at 11°.—NH_4A'. S. ·95 at 11°.—BaA'_2aq. S. (of BaA'_2) ·0204 at 10·5°.—$CaA'_2$3aq. S. (of CaA'_2) ·159 at 11°.—$PbA'_2$3aq. S. (of PbA'_2) ·0184 at 11°.—AgA'½aq. S. (of AgA') ·146 at 11°.—AgA'aq.

Chloride $C_6HBr_4SO_2Cl$. [120°].

Amide $C_6HBr_4SO_2NH_2$. Turns brown at 210°.

Penta-bromo-benzene sulphonic acid $C_6Br_5SO_3H$. S. ·548 at 10°. From either tetra-bromo-amido-benzene sulphonic acid by diazo- reaction (Beckurts, *A.* 181, 226; Heinzelmann a. Spiegelberg, *A.* 197, 306; Langfurth, *A.* 191, 205). Needles or plates (containing 7aq).

Salts.—NH_4A'.—KA'aq. S. (of KA') ·116 at 10·5°.—$CaA'_2$4aq. S. (of CaA'_2) ·78 at 14°.—BaA'_2aq. S. (of BaA'_2) ·0088 at 13°.—BaA'_2 1½aq. AgA' 1½aq.

Chloride $C_6Br_5SO_2Cl$. [154°].

Amide $C_6Br_5SO_2NH_2$. Decomposes at 250°.

BROMO-BENZIDINE *v.* BROMO-DI-AMIDO-DIPHENYL.

***o*-BROMO-BENZOIC ACID** $C_7H_5BrO_2$ *i.e.* $C_6H_4Br.CO_2H$ [1:2]. Mol. w. 201. [148°] (Z.; J. a. W.); [150°] (R.).

Formation.—1. From *o*-amido-benzoic acid (Richter, *B.* 4, 465).—2. By heating $C_6H_4Br(NO_2)$ [1:3] with KCy at 180° (R.).—3. By oxidation of *o*-bromo-toluene (Zincke, *B.* 7, 1502; Rahlis, *A.* 198, 99), *o*-bromo-diphenyl (Schultz, *A.* 207, 353), or *o*-bromo-benzyl alcohol (Jackson a. White, *Am.* 2, 316).

Properties.—Long needles (from water); m. sol. water, v. sol. alcohol, and ether; slightly volatile with steam.

Salts.—BaA'_2.—$BaA'_2$2HOEt.—$CaA'_2$3aq.—KA'2aq.—ZnA'_2—PbA'_2HOEt.—CuA'_2aq. [257°].—$HOCuA'$.

Methyl ether MeA'. (247°).

Ethyl ether EtA'. (255°).

Anilide $C_6H_4Br.CONPhH$. [142°].

***m*-Bromo-benzoic acid** $C_6H_4BrCO_2H$ [1:3]. [155°]. (280°).

Formation. — 1. From AgOBz and Br (Peligot, *A.* 28, 246; Angerstein, *A.* 158, 2).—2. From benzoic acid and Br in the sunshine (Herzog, *N. Br. Arch.* 23, 16) or by heating them with water at 100° or 160° (Reinecke, *Z.* 1865, 116; 1869, 100; Hübner, *A.* 143, 233; 149, 131).—3. By heating benzamide with Br and water (Reinecke, *Z.* 1866, 367; Friedburg, *A.* 158, 26).—4. From *m*-amido-benzoic acid by diazo- reaction (Griess, *A.* 117, 25; Hübner, *A.* 222, 100).—5. From $C_6H_4Br(NO_2)$ [1:4], KCy, and alcohol at 200° (Richter, *B.* 4, 464).—6. By oxidation of *m*-bromo-toluene (Wroblewsky, *Z.* [2] 5, 332; *A.* 168, 156) or *m*-bromo-benzyl alcohol (Jackson, *Am.* 1, 93).—7. By the action of a hot solution of cuprous cyanide in potassium cyanide upon *m*-bromo-diazo-benzene-chloride (from *m*-bromaniline), and saponification of the crude nitrile (Sandmeyer, *B.* 18, 1496).—8. From *m*-di-bromo-benzene, ClCO₂Et, and Na (Wurster, *A.* 176, 149).

Properties.—Crystalline; very slightly volatile with steam; sl. sol. water, v. sol. alcohol.

Reactions.—1. *Potash-fusion* gives *m*- and a little *o*-oxy-benzoic acid (Richter, *Z.* 1869, 457; Barth, *A.* 159, 236).—2. The K salt fused with *sodium formate* gives isophthalic acid (V. Meyer a. Ador, *A.* 159, 15).

Salts.—$CaA'_2$3aq.—$BaA'_2$4aq: needles.

Methyl ether MeA'. [32°].

Ethyl ether EtA'. (259°).

Phenyl ether PhA'. [65°].

Chloride $C_6H_4Br.COCl$. (239°).

Amide $C_6H_4Br.CONH_2$. [150°].

Nitrile C_6H_4BrCN. [38°]. (225°). From the amide (Engler, *B.* 4, 708). Formed also by the action of a hot solution of potassium cuprous cyanide upon *m*-bromo-diazo-benzene chloride (from *m*-bromaniline) (Sandmeyer, *B.* 18, 1496).

***p*-Bromo-benzoic acid** $C_6H_4Br.CO_2H$ [1:4]. [251°]. *Formation.*—1. By oxidation of *p*-bromo-toluene (Hübner, *A.* 143, 247; Jackson a. Rolfe, *Am.* 9, 84), *p*-bromo-ethyl-benzene (Fittig a. König, *A.* 144, 283), or *p*-bromo-benzyl bromide (Jackson, *Am.* 1, 93).—2. From *p*-bromo-aniline *viâ* *p*-bromo-thio-carbimide, the latter when heated with copper at 190° giving *p*-bromo-benzonitrile (Weith a. Landolt, *B.* 8, 715).

Properties.—Small needles (from ether) or

plates (from water). V. sl. sol. water, v. sol. alcohol and ether.—AgA'.

Ethyl ether EtA' (236° uncor.) at 713 mm. Formed, together with *p*-bromo-benzyl-alcohol, by boiling *p*-bromo-benzyl bromide with alcoholic KOH (Elbs, *J. pr.* [2] 34, 341).

Phenyl ether PhA'. [117°]. Scales.

Pyrogallyl ether $C_6H_3A'_3$. [140°].

Chloride. [30°]. (246°). Needles.

Amide $C_6H_4Br.CONH_2$. [186°].

Anilide $C_6H_4Br.CONPhH$. [197°]. Plates. On nitration it gives a dinitro-derivative. [214°]. (Raveill, *A.* 222, 178).

Anhydride $(C_6H_4BrCO)_2O$. [213°]. From *p*-bromo-benzoyl chloride and sodium *p*-bromo-benzoate (J. a. R.). Minute oblong rectangular plates (from $CHCl_3$). Insol. water. Converted by hot HOEt into the ethyl ether.

Di-bromo-benzoic acid $C_6H_3Br_2CO_2H$ [1:2:3] [147°]. From (α)-bromo-amido-benzoic acid [1:2:3] by diazo-reaction (Hübner, *A.* 222, 105). From (1, 2, 3)-di-bromo-toluene (Nevile a. Winther, *B.* 13, 965). Silky needles (from water). V. sol. hot water. Heated with H_2SO_4 (3 vols.) and H_2O (1 vol.) at 225° it gives *o*-di-bromo-benzene [218·5°].

Salts. $BaA'_2 4\frac{1}{2}aq$. S. (of BaA'_2) 4·44 at 16°. - $SrA'_2 4aq$.—A'CuOH.—KA'*x*aq.

This acid is perhaps identical with the di-bromo-benzoic acid [148°] prepared from *o*-nitro-benzoic acid, Br, and water at 200° (Claus a. Lade, *B.* 14, 1170).

Di-bromo-benzoic acid $C_6H_3Br_2CO_2H$ [1:4:3]. [153°]. From (β)-bromo-amido-benzoic acid [1:4:3] by passing nitrous acid gas into a mixture of the acid, HBr, glacial acetic acid and alcohol (Hübner, *A.* 222, 108). From nitro-*p*-di-bromo-benzene and alcoholic KCy (Richter, *B.* 7, 1146). From (1, 4, 3)-di-bromo-toluene by oxidation (Nevile a. Winther, *B.* 13, 963). Long silky needles (from water). Volatile with steam. Heated with H_2SO_4 (3 vols.) and water (1 vol.) at 225° gives *p*-di-bromo-benzene [89°].

Salts.—$BaA'_2 1\frac{1}{2}aq$.—$SrA'_2 4aq$.—ZnA'_2.—$CaA'_2 3\frac{1}{2}aq$.—KA'aq.

This acid is probably identical with the di-bromo benzoic acid [153°] from *o*-nitro benzoic acid, Br, and water at 200° (Claus a. Lade, *B.* 14, 1170).

Di-bromo-benzoic acid $C_6H_3Br_2CO_2H$ [1:3:2]?. [150°-167°]. By oxidising di-bromo-toluene from di-bromo-*m*-toluidine, [35°] (Nevile a. Winther, *C. J.* 37, 441).

Di-bromo-benzoic acid $C_6H_3Br_2CO_2H$ [1:3:4]. [169°]. By oxidising di-bromo-toluene from di-bromo-*m*-toluidine [76°] (Nevile a. Winther, *C. J.* 37, 441).

Di-bromo-benzoic acid $C_6H_3Br_2CO_2H$ [1:3:5] [207°-210°] (N. a. W.); [209°] (R.); [214°] (H.).

Formation.—1. By oxidation of di-bromo-toluene [39°] from di-bromo-*p*-toluidine [73°] (Nevile a. Winther, *C. J.* 37, 437).—2. From *m*-di-bromo-benzene by nitration and treatment with alcoholic KCy at 250° (V. v. Richter, *B.* 8, 1423).—3. From di-brominated *p*-amido-benzoic acid (Beilstein a. Geitner, *A.* 139, 4).—4. From $C_6H_3Br(NH_2)CO_2H$, aqueous HBr (S.G. 1·48), glacial acetic acid and N_2O_3 at 15° (Hesemann a. Köhler, *A.* 222, 171).

Properties.—Plates (from alcohol) Needles (from other solvents).

Salts.—$BaA'_2 4aq$.—$CaA'_2 5aq$.—$CdA'_2 4aq$—$CaA'_2 6aq$.—NaA'aq.—$CdA'_2 4aq$.

Di-bromo-benzoic acid $C_6H_3Br_2CO_2H$ [1:3:x] [223°-227°]. Formed by heating benzoic acid with Br and water at 220° (Angerstein, *A.* 158, 10). Needles.—$BaA'_2 2aq$.

Di-bromo-benzoic acid $C_6H_3Br_2CO_2H$ [1:2:4] [229°-230°] (B.); [233°] (N. a. W.).

Formation.—1. $C_6H_3Br(NH_2)CO_2H$ [4:3:1] is treated with ether and N_2O_3 and the diazo-derivative treated with HBr (Burghard a. Beutnagel *A.* 222, 181).—2. By oxidising the corresponding di-bromo-toluene from brominated *p*-toluidine (Nevile a. Winther, *C. J.* 37, 439).—3. A product of the action of Br on *p*-nitro-benzoic, or (1, 2, 4)-di-nitro-benzoic, acid (Halberstadt, *B.* 14, 908, 2215).

Properties.—Colourless needles (from water), tables (from alcohol).

Salts.—$BaA'_2 4aq$.—$SrA'_2 4aq$.—HOCuA'.—AgA'.—KA'*x*aq.

Ethyl ether EtA'. [38°].

Amide $C_6H_3Br_2CONH_2$. [151°-152°].

Tri-bromo-benzoic acid $C_6H_2Br_3(CO_2H)$. [235°]. From *m*-bromo-benzoic acid and Br (Reinecke, *Z.* [2] 5, 110). Tufts of slender silky needles; v. sl. sol. water.—NH_4A'.—$CaA'_2 5aq$.

Tri-bromo-benzoic acid $C_6H_2Br_3CO_2H$. [1:3:5:6]. [187°]. From tri-brominated *m*-amido-benzoic acid (Vollbrecht, *B.* 10, 1708). Needles.—$BaA'_2 5\frac{1}{2}aq$.

Tri-bromo-benzoic acid $C_6H_2Br_3CO_2H$. [195°]. From (1, 2, 4)-di-bromo-benzoic acid [229°] by nitration, reduction, and diazotisation (Smith, *B.* 10, 1706). Needles (from alcohol).—$BaA'_2 5aq$.

Tri-bromo-benzoic acid $C_6H_2Br_3CO_2H$. [178°]. From (1, 4, 5)-bromo-amido-benzoic acid (Lawrie, *B.* 10, 1705). Needles.—$BaA'_2 3aq$.

Penta-bromo-benzoic acid $C_6Br_5CO_2H$. [235°]. From tri-bromo-benzoic acid and Br at 200° (Reinecke, *Z.* [2] 5, 110). Thin plates or flat needles (from alcohol); thick needles (from benzene); v. sl. sol. water.—NH_4A'.—$CaA'_2 6aq$.

Nitrile C_6Br_5CN. [above 300°]. Obtained by brominating benzonitrile (Merz a. Weith, *B.* 16, 2892).

o-**BROMO-BENZOIC ALDEHYDE** $C_6H_4Br.CHO$ [1:2]. A heavy oil; formed by boiling *o*-bromo-benzyl bromide with aqueous lead nitrate (Jackson a. White, *Am.* 3, 33; *P. Am. A.* 15, 269).

m-**Bromo-benzoic aldehyde** $C_6H_4Br.CHO$ [1:3]. Oil (J. a. W.).

p-**Bromo-benzoic aldehyde** $C_6H_4Br.CHO$ [1:4]. [57°] (Jackson a. White, *B.* 11, 57).

BROMO-BENZOIC SULPHINIDE *v.* BROMO-SULPHO-BENZOIC ACID.

BROMO-BENZOPHENONE $C_{13}H_9BrO$ *i.e.* $C_6H_5.CO.C_6H_4Br$. [81·5°]. From benzoic acid, bromo-benzene and P_2O_5 at 190° (Kollarits a. Merz, *B.* 6, 547).

BROMO-BENZOYL CHLORIDE *v. Chloride of* BROMO-BENZOIC ACID.

BROMO-DI-BENZYL *v.* BROMO-DI-PHENYL-ETHANE.

o-**BROMO-BENZYL ALCOHOL** C_7H_7BrO *i.e.* $C_6H_4Br.CH_2.OH$. [80°]. Prepared by digesting *o*-bromo-benzyl acetate with aqueous ammonia at 160°. Crystallises in white needles. Sol. hot water, ligroin, alcohol, ether, benzol, and CS_2.

Volatile with steam (Jackson a. White, *Am.* 2, 316; *B.* 13, 1218).

m-Bromo-benzyl alcohol $C_6H_4Br.CH_2OH$. From *m*-bromo-benzyl bromide and water at 130° (J. a. W.).

p-Bromo-benzyl alcohol $C_6H_4BrCH_2OH$. [77°]. Prepared by boiling *p*-bromo-benzyl bromide with water for 3 days. Long elastic transparent needles. Sol. alcohol, ether, benzene, and CS_2 (Jackson a. Lowery, *Am.* 3, 246; *B.* 10, 1209).

o-BROMO-BENZYL-AMINE $C_6H_4Br.CH_2NH_2$. Prepared by acting on *o*-bromo-benzyl bromide with alcoholic ammonia at 100° for 2 hours (Jackson a. White, *Am.* 2, 318). Colourless oil; sol. ether. Salts.—B'HCl: [208°]; needles.—$B'_2H_2PtCl_6$.—$B'_2H_2CO_3$. [95°].

p-Bromo-benzyl-amine $C_6H_4Br.CH_2NH_2$. From *p*-bromo-benzyl bromide and cold alcoholic NH_3 (Jackson a. Lowery, *Am.* 3, 251). Oil; volatile with steam.—B'HCl [160°].—$B'_2H_2PtCl_6$.—$B'_2H_2CO_3$ [131°–133°]: small prisms.

Di-o-bromo-di-benzyl-amine $(C_6H_4Br.CH_2)_2NH$. [36°]. From *o*-bromo-benzyl bromide and alcoholic NH_3 at 100°. Trimetric crystals; insol. water (Jackson a. White, *Am.* 2, 318; *B.* 13, 1219). B'HCl [166°].—$B'_2H_2PtCl_6$.

Di-p-bromo-di-benzyl-amine $(C_6H_4Br.CH_2)_2NH$. [50°].—B'HCl [183°].—$B'_2H_2PtCl_6$ (J. a. W.).

Tri-o-bromo-tri-benzyl-amine $(C_6H_4Br.CH_2)_3N$. [122°]. From *o*-bromo-benzyl bromide and alcoholic NH_3 at 100° (J. a. W.). Small prisms.—$B'_2H_2PtCl_6$.

Tri-p-bromo-tri-benzyl-amine $(C_6H_4Br.CH_2)_3N$. Crystals (from ligroïn) [92°]; (from ether) [78°]. Slender needles; the hydrochloride could not be obtained.—B'HBr. [270°]; insol. water.—$B'_2H_2PtCl_6$ (Jackson a. Lowery, *Am.* 3, 252).

o-BROMO-BENZYL BROMIDE $C_6H_4Br.CH_2Br$ [1:2]. [30°]. (250°–260°). *Di-bromo-toluene.* Prepared by brominating *o*-bromo-toluene (Jackson, *Am.* 1, 93; 2, 315; *B.* 13, 1218). Very pungent; volatile with steam. Converted in ethereal solution by Na into anthracene, phenanthrene, *s*-di-phenyl-ethane, and other products.

m-Bromo-benzyl bromide $C_6H_4Br.CH_2Br$ [1:3]. [41°]. From *m*-bromo-toluene and Br (Jackson, *Am.* 1, 93; *B.* 9, 932). Pungent plates; slightly volatile with steam; very volatile with ether-vapour.

p-Bromo-benzyl bromide $C_6H_4Br.CH_2Br$ [1:4]. [62°]. Formed by brominating *p*-bromo-toluene or benzyl bromide (Jackson, *Am.* 1, 93; Schramm, *B.* 17, 2922; 18, 350). Needles (from alcohol); volatile with steam; very pungent. Alcoholic KOH forms *p*-bromo-benzyl alcohol and *p*-bromo-benzoic ether (Elbs, *J. pr.* [2] 34, 340).

BROMO-BENZYL CYANIDE *v.* *Nitrile of* BROMO-PHENYL-ACETIC ACID.

BROMO-BENZYLIDENE-PHTHALIMIDINE $C_{15}H_{10}ONBr$. *Phthalimidyl-bromo-benzyl.* [210°]. Glistening needles. Formed by the action of bromine upon deoxybenzoïn-carboxylamide $C_6H_4(CO.NH_2)CO.CH_2.C_6H_5$ dissolved in chloroform (Gabriel, *B.* 18, 2435).

TETRA-BROMO-BENZYLIDENE-DI-TOLYL-DIAMINE $(PhCH)_2(NC_6H_2Br_2Me)_2$. [160°–165°]. From benzylidene-di-*p*-tolyl-diamine and Br (Mazzara, *G.* 10, 370).

p-BROMO-BENZYL MERCAPTAN $C_6H_4Br.CH_2SH$. [25°]? From *p*-bromo-benzyl bromide and alcoholic KHS (Jackson a. Hartshorn, *Am.* 5, 268). Crystalline mass; insol. water and glacial HOAc; sol. alcohol, ether, and benzene.—$Hg(SC_7H_6Br)_2$: sol. hot alcohol.

DI-BROMO-BENZYL-PHENOL $C_{13}H_{10}Br_2.OH$. [175°]. From benzyl-phenol in CS_2 and Br (Paterno a. Fileti, *G.* 3, 251). Amorphous.

BROMO-o?-BENZYL-PHENOL SULPHONIC ACID $C_6H_5.C_6H_2(OH)BrSO_3H$. Salt. KA'. From Br and $C_6H_5.C_6H_3(OH)SO_3K$ (Rennie, *C. J.* 49, 409).

Bromo-p-benzyl-phenol sulphonic acid $C_7H_7.C_6H_2(OH)Br.SO_3H$ [1:4:x:2].

Salt.—KA' (Rennie, *C. J.* 41, 35).

p-BROMO-BENZYL SULPHIDE $(C_6H_4BrCH_2)_2S$. [59°]. Prepared by boiling *p*-bromo benzyl bromide with alcoholic Na_2S. Large thin plates. Aromatic odour. Insol. water. Sol. ether, benzene, and CS_2 (Jackson a. Hartshorn, *Am.* 5, 267).

p-Bromo-benzyl disulphide $(C_6H_4BrCH_2)_2S_2$ [88°]. Prepared by exposing the mercaptan to air, and also by acting on *p*-bromo-benzyl bromide with alcoholic Na_2S_2. Needles. Insol. water; sol. ether, benzene, and CS_2 (Jackson a. Hartshorn, *Am.* 5, 269).

p-BROMO-BENZYL SULPHOCYANIDE $C_6H_4Br.SCN$. [25°]. From *p*-bromo-benzyl bromide and potassium sulphocyanide. The *o*-isomeride is an oil (Jackson a. Lowery, *B.* 10, 1209; *Am.* 3, 250).

DI-p-BROMO-DI-BENZYL SULPHONE $(C_6H_4Br.CH_2)_2SO_2$. [183°]. From the sulphide and CrO_3 in HOAc. Needles (Jackson a. Hartshorn, *Am.* 5, 269).

BROMO-BENZYL SULPHONIC ACID *v.* BROMO-TOLUENE SULPHONIC ACID.

DI-BROMO-BETORCIN $C_6Br_2Me_2(OH)_2$ [155°]. From tetra-bromo betorcin and HI. Also by boiling a mixture of betorcin (3 pts.), bromine (8 pts.) and CS_2 (100 vols.). The product is recrystallised from light petroleum (Stenhouse a. Groves, *C. J.* 37, 401). Long needles.

Tetra-bromo-betorcin $C_6Br_2Me_2(OBr)_2$. [101°]. From bromine (5 pts.), water (100 vols.) and betorcin (1 pt.). Dissolved in water (50 pts.). Crystallised from light petroleum (S. a. G.).

Large colourless prisms. V. sol. ether, benzene and CS_2, less so in petroleum.

BROMO-BRASILIN $C_{16}H_{13}BrO_5$. Obtained by brominating acetyl-brasilin and saponifying the product. Glistening red plates. V. sol. water. Dissolves in KOH with a red colour.

Tetra-acetyl derivative $C_{16}H_9Br(OAc)_4O$. [204°] (Buchka a. Erck, *B.* 17, 685; 18, 1140).

Tri-bromo-brasilin $C_{16}H_{11}Br_3O_5$.

Tetra-acetyl derivative $C_{16}H_7Br_3(OAc)_4O$. [147°]. Small white needles; very oxidisable (B. a. E.).

Tetra-bromo-brasilin $C_{16}H_{10}Br_4O_5$. Slender red needles. Dissolves in alkalis with a violet colour. Obtained by bromination of brasilin.

Tetra-acetyl derivative $C_{16}H_6Br_4(OAc)_4O$. [222°] (B. a. E.).

BROMO-BUTANE *v.* BUTYL BROMIDE.

ω-α-Di-bromo-butane $C_4H_8Br_2$ *i.e.* $CH_2Br.CHBr.CH_2.CH_3$. *Butylene bromide.* (166°). S.G. $\frac{20}{0}$ 1·820. Formed by the action of Br on *n*-butylene or *n*-butyl bromide (Wurtz, *A.* 152, 23,

Linnemann, *A.* 161, 199; Grabowsky a. Saytzeff, *A.* 179, 332). Na forms CH_2:CH.CH_2CH_3.

αβ-Di-bromo-butane CH_3.CHBr.CHBr.CH_3. (158°). S.G. ° 1·82. From CH_3.CH:CH.CH_3 and Br. Converted by PbO and excess of water at 150° into methyl ethyl ketone (Wurtz, *A.* 144, 236; Eltekoff, *J. R.* 10, 219).

Di-bromo-isobutane $(CH_3)_2CBr.CH_2Br$. *Isobutylene bromide.* (149°). S.G. $\frac{14}{}$ 1·8; $\frac{15}{15}$ 1·7434; $\frac{25}{25}$ 1·7308. M. M. 11·890 at 14·7° (Perkin). From isobutylene and Br (Linnemann, *A.* 162, 36). By heating with excess of water at 150° it is converted into isobutyric aldehyde; if PbO is also present some di-oxy-isobutane is also formed (Eltekoff, *J. R.* 10, 214).

Di-bromo-butane $C_4H_8Br_2$. (155°-162°). Formed by brominating butane (Carius, *A.* 126, 215).

Tri-bromo-isobutane $C_4H_7Br_3$ *i.e.* $(CH_2Br)_2CBr.CH_3$. (173°-183°) at 235 mm. S.G. $\frac{17}{17}$ 2·15. From isobutylene and Br (Norton a. Williams, *Am.* 9, 88).

Tri-bromo-isobutane $C_4H_7Br_3$ *i.e.* $(CH_3)_2CBr.CHBr_2$. (155°-161°) at 235 mm. From $(CH_3)_2C$:CHBr and Br (N. a. W.).

Tri-bromo-butane $C_4H_7Br_3$. (208°-215°). From bromo-butylene (82°-92°) (Caventou, *A.* 127, 93).

Tetra-bromo butane $C_4H_6Br_4$ *i.e.* $CH_2Br.CHBr.CHBr.CH_2Br$. *Butinene- or pyrrolylene- tetra-bromide.* [119°]. Formed by combination of bromine with the butinene from di-methyl-pyrrolidine or from erythrite. From erythrite, vinyl-ethylene, or gas oils (Caventou, *A.* 127, 93; *B.* 6, 70; Henninger, *B.* 6, 70; Grimaux a. Cloez, *C. R.* 104, 1446; *Bl.* [2] 48, 31). From the gas obtained by passing acetylene mixed with ethylene through a red-hot tube (Prunier, *Bl.* [2] 20, 72). On distillation it is partially converted into the following body. Colourless needles (from alcohol). Insol. cold petroleum-ether (Ciamician a. Magnaghi, *B.* 19, 569).

Tetra-bromo-butane $CH_3.CBr_2.CBr_2.CH_3$ (?) [40°]. *Erythrene isobromide. Erythrite tetrabromhydrin.* Formed, together with the isomeride [119°], by combining butinene from erythrite with bromine. Large colourless trimetric prisms or tables, $a:b:c$ = ·9776:1:1·682 (Ciamician a. Magnaghi, *B.* 19, 569). V. sol. ether, alcohol, and petroleum-ether. Alcoholic KOH converts both this and the preceding into the same di-bromo-butinene $C_4H_4Br_2$, which rapidly polymerises. The latter absorbs Br, forming $C_4H_4Br_4$ [67°] and $C_4H_4Br_6$ [170°].

Tetra-bromo-butane $C_4H_6Br_4$. From Br and di-bromo-butylene (140°-150°) from fusel oil *viâ* butylene (Caventou, *A.* 127, 93). Crystalline; decomposes at 200°.

Tetra-bromo-butane $CH_3.CH_2.CBr_2.CHBr_2$. From butinene prepared from methyl ethyl ketone by successive treatment with PCl_5 and alcoholic KOH. Sublimes at 105° (Bruylants, *B.* 8, 410).

Tetra-bromo-isobutane $C_4H_6Br_4$. [205°]. From di-bromo-isobutylene (155°) (Norton a. Williams, *Am.* 9, 87).

Hexa-bromo-butane $C_4H_4Br_6$. [109°]. Obtained by brominating isobutyl bromide at 170°. The yield is 90 p.c. of the theoretical (Merz a. Weith, *B.* 11, 2245).

Hexa-bromo-butane $C_4H_4Br_6$ *i.e.* $Br_2CHBr.CHBr.CHBr_2$. S.G. is 2·9. Formed together with the following, by heating erythrite tetrabromhydrin with Br at 180° (Colson, *Bl.* [2] 48, 52). Liquid; v. sol. ether, sl. sol. alcohol. Dilute KOH at 130° converts it into potassium erythrate.

Hexa-bromo-butane $C_4H_4Br_6$. [170°]. S.G. 3·4. Formed in small quantity as above (C.). Pearly scales, sl. sol. ether and alcohol. Fuming HNO_3 forms an oil $C_4H_3(NO_2)Br_2(NO_3)_2$, S.G. 1·81.

DI-BROMO-BUTYL ALCOHOL $C_4H_8Br_2O_2$ *i.e.* $CH_3.CHBr.CHBr.CH_2OH$. Oil. From butenyl alcohol $CH_3.CH$:CH.CH_2OH and Br (Lieben a. Zeisel, *M.* 1, 828). Boiling water forms tri-oxy-butane.

ωα-DI-BROMO-*n*-BUTYL-BENZENE $C_{10}H_{12}Br_2$ *i.e.* $C_6H_5.CH_2.CH_2.CHBr.CH_2Br$. From phenyl-butylene and Br (Aronheim, *A.* 171, 229). Oil. *Reactions.*—1. Red-hot soda-lime forms naphthalene.—2. HNO_3 forms a little bromo-phenyl-propionic acid.

βγ-Di-bromo-*n*-butyl-benzene $C_6H_5.CHBr.CHBr.CH_2CH_3$. [67°]. From butenyl-benzene and Br (Perkin, *C. J.* 32, 668).

γγ-Di-bromo-*n*-butyl benzene $C_6H_5.CBr_2.CH_2.CH_2.CH_3$ (?). From butyl-benzene and Br in sunlight. Unstable oil (Schramm, *B.* 18, 1276).

Di-bromo-*n*-butyl-benzene $C_{10}H_{12}Br_2$. [70°]. From *n*-butyl-benzene and Br first in sunlight, then heated in the dark (Radziszewski, *B.* 9, 261).

αβ-Di-bromo-isobutyl-benzene $C_6H_5.CHBr.CBrMe_2$. From phenyl-isobutylene and Br (Perkin, *C. J.* 35, 138).

Tri-bromo-isobutyl benzene $C_{10}H_{11}Br_3$. [64°]. From the preceding by successive treatment with alcoholic KOH and Br (P.).

BROMO-BUTYLENE C_4H_7Br *i.e.* $(CH_3)_2C$:CHBr. (91°). *Isocrotyl bromide.* From isobutylene bromide and alcoholic KOH (Butlerow, *Z.* 1870, 524). Alcoholic KOH at 170° forms $(CH_3)_2C$:CH.OEt. Moist Ag_2O at 100° gives isobutyric acid. NH_3 has no action.

Bromo-butylene C_4H_7Br. (82°-92°). From fusel oil butylene by successive treatment with Br and alcoholic KOH (Caventou, *A.* 127, 93).

Bromo-butylene C_4H_7Br. (87° i.V.). From di-bromo-methyl-ethyl-acetic acid and aqueous Na_2CO_3 (Jaffé, *A.* 135, 300; Pagenstecher, *A.* 195, 126).

Bromo-butylene C_4H_7Br. (97°). Formed by boiling the di-bromide of angelic acid with water (Jaffé, *A.* 135, 300).

Di-bromo-iso-butylene $C_4H_6Br_2$. (155°). From tri-bromo-iso-butane (155°-161°) at 235 mm. (Norton a. Williams, *Am.* 9, 87).

Di-bromo-butylene $C_4H_6Br_2$. (140°-150°). From tri-bromo-butane (208°-215°). Forms a crystalline di-bromide $C_4H_6Br_4$ which decomposes without melting at 200° (Caventou, *A.* 127, 93).

Di-bromo-butylene $C_4H_6Br_2$. (148°-158°). From crotonylene and Br (Caventou, *A.* 127, 349).

Di-bromo-butylene $C_4H_6Br_2$. From tetra-bromo-butane [119°] (from erythrite) and alcoholic KOH. Rapidly polymerises. Combines readily with bromine (Grimaux a. Cloez, *Bl.* [2] 48, 31).

Di-bromo-butylene $C_4H_6Br_2$ *i.e.* CH_2:CH.CHBr.CH_2Br. (190°-200°). From the

oils deposited by compressed gas, by adding less than the calculated quantity of Br and fractionally distilling. Combines readily with Br, forming $C_4H_6Br_4$ [119°] (G. a. C.).

Hexabromobutylene $C_4Br_6H_2$. [53°]. Prepared by further bromination of hexabromisobutane (Merz a. Weith, *B.* 11, 2240).

α-BROMO-*n*-BUTYRIC ACID $C_4H_7BrO_2$ *i.e.* $CH_3.CH_2.CHBr.CO_2H$. (214°-217°). (110°) at 8 mm. S.G. $\frac{15}{}$ 1·54. S. 7.

Formation.—1. By heating butyric acid with Br at 140°; or by the action of Br on silver butyrate (Friedel a. Machuca, *A.* 120, 279; *Suppl.* 2, 70; Gorup-Besanez a. Klinksieck, *A.* 118, 248; Naumann, *A.* 119, 115; Ley, *J. R.* 9, 129; Urech, *A.* 165, 93; Tupoleff, *A.* 171, 249). — 2. From crotonic acid and HBr.—3. From the bromide and water (Kaschirski, *C. C.* 1881, 278).

Properties.—Oil; mixes with alcohol and ether. NEt_3, whether dry or in aqueous solution, forms α oxy-butyric acid (Duvillier, *Bl.* [2] 48, 3). NaOHAq acts similarly.

Salts.—PbA'_2.—$PbA'_2 2PbO$.—AgA'.

Methyl ether MeA'. (165°-172°).

Ethyl ether EtA'. (178°) (Lovén, *J. pr.* [2] 33, 102). S.G. $\frac{12}{}$ 1·345. Dry NaOEt forms an ether $C_8H_{10}O_4(OEt)_2$ (252°) (Krestownikoff, *A.* 208, 348).

Bromide $C_4H_6BrO.Br$. (173°). From butyryl bromide and Br.

β-Bromo-butyric acid $CH_3.CHBr.CH_2.CO_2H$. Formed in small quantity in the preparation of the α- acid from crotonic acid and HBr (Hemilian, *A.* 174, 325).

γ-Bromo-butyric acid $CH_2Br.CH_2.CH_2.CO_2H$. [33°]. From butyro-lactone and HBr (Henry, *C. R.* 102, 368). Tables or plates; sl. sol. water, v. sol ether.

Methyl ether MeA'. (187°). S.G. $\frac{0}{}$ 1·45.

Ethyl ether EtA'. (197°). S.G. $\frac{0}{}$ 1·36.

α-Bromo-isobutyric acid $(CH_3)_2CBr.CO_2H$. [48°]. (199°). S.G. $\frac{60}{}$ 1·52. From isobutyric acid and Br (Markownikoff, *A.* 153, 229; Hell a. Waldauer, *B.* 10, 448). Tables. Boiling water converts it into α-oxy-isobutyric acid, KHS acts similarly (Lovén, *J. pr.* [2] 33, 105); boiling baryta-water forms also $CH_2:CMe.CO_2H$ (Engelhorn, *A.* 200, 68).

Ethyl ether EtA'. (164° cor.). S.G. $\frac{0}{}$ 1·13. Oil; smelling of raspberries and peppermint (Markownikoff, *A.* 182, 336; Hell a. Wittekind, *B.* 7, 320; Lovén, *J. pr.* [2] 33, 106).

Bromide $(CH_3)_2CBr.COBr$. (163°).

β-Bromo-isobutyric acid $CH_2Br.CHMe.CO_2H$. [22°]. From α-methyl-acrylic acid and cold conc. HBr. Crystals (from CS_2). Boiling alkalis convert it into α-methyl-acrylic acid and a little propylene (Fittig a. Engelhorn, *A.* 200, 65).

αα-Di-bromo-butyric acid
$CH_3.CH_2.CBr_2.CO_2H$. (140°) at 3 mm. S. 3. S.G. 1·96. From bromo-butyric acid and bromine (Schneider, *J.* 1861, 458; Michael a. Norton, *Am.* 2, 15; Otto a. Fromme, *A.* 239, 275). Thick oil. Water or baryta-water at 120° forms α-bromo-crotonic acid (Erlenmeyer a. Müller, *B.* 15, 49). Converted by reduced silver into di-ethyl-maleïc or xeronic acid $CO_2H.CEt:CEt.CO_2H$, butyric acid being formed.

αβ-Di-bromo-butyric acid
$CH_3.CHBr.CHBr.CO_2H$. [87°].

Preparation.—From Br and crotonic or isocrotonic acid dissolved in CS_2 (Körner, *A.* 137, 234; Michael a. Norton, *Am.* 2, 12; *B.* 14, 1202; C. Kolbe, *J. pr.* 133, 386).

Properties.—Large transparent prisms (from CS_2); sol. alcohol, ether, and hot water.

Reactions.—1. Boiled with *water* or Na_2CO_3 it gives β-bromo-propylene, bromo-oxy-butyric acid, di-oxy-butyric acid, and bromo-crotonic acid. Water gives chiefly bromo-oxy-butyric acid; Na_2CO_3 gives more bromo-propylene, but no propionic aldehyde. — 2. Warmed with a solution of NaOH it gives bromo-crotonic acid.

Di-bromo-iso-butyric acid
$CH_2Br.CBrMe.CO_2H$. [48°].

Preparation.—By adding Br to methacrylic acid dissolved in CS_2 (C. Kolbe, *J. pr.* [2] 25, 373). Long prisms (from CS_2). Boiling with *water* or Na_2CO_3 produces CO_2, acetone, some propionic aldehyde, a very little bromo-methacrylic acid [63°], and bromo-oxy-iso-butyric acid (*q.v.*). Warmed with solution of NaOH it gives bromo-methacrylic acid and HBr.

Tri-bromo-butyric acid $C_4H_5Br_3O_2$ *i.e.* $CH_3.CBr_2.CHBr.CO_2H$? [114°]. From β-bromo-crotonic acid in CS_2 and Br (Michael a. Norton, *Am.* 2, 14). Rhombic plates; sol. alcohol and hot water; sublimes readily.

Tri-bromo-butyric acid $C_4H_5Br_3O_2$ *i.e.* $CH_3.CHBr.CBr_2.CO_2H$? [111°]. From α-bromo-crotonic acid and Br. V. sol. water and alcohol (M. a. N.).

Tri-bromo-isobutyric acid $C_4H_5Br_3O_2$. From bromo-α-methyl-acrylic acid and Br (Cahours, *A. Suppl.* 2, 349). Prisms.

Tetra-bromo-butyric acid $C_4H_4Br_4O_2$. [115°]. From mucobromic acid and Br (Limpricht, *A.* 165, 293). Monoclinic tables; sl. sol. water.

Tetra-bromo-isobutyric acid $C_4H_4Br_4O_2$. From di-bromo-α-methyl-acrylic acid and Br (C.).

BROMO-ISO-BUTYRIC *para*-ALDEHYDE $((CH_3)_2CBr.CHO)_n$. [129°]. When the product of the action of NH_3 on iso-butyric aldehyde (*q.v.*) is distilled a product $C_8H_{15}N$ is got. This must be combined with bromine, and the compound, $(CH_3)_2CH.CH:N.CHBr.CBr(CH_3)_2$, after keeping for 3 months, is decomposed by water (Lipp, *A.* 211, 353). Needles (from alcohol). Insol. water, acids or alkalis, v. sol. ether, m. sol. alcohol. Does not reduce ammoniacal $AgNO_3$.

BROMO-CATECHOL *v.* BROMO-PYROCATECHIN.

BROMO-CAFFEÏNE $C_8H_9BrN_4O_2$. [206°]. Caffeïne combines with Br forming the orange-red bromide $C_8H_{10}N_4O_2Br_2$, which is decomposed at 150° into HBr and bromo-caffeïne (Fischer, *B.* 14, 639; Schultzen, *Z.* 1867, 614; Maly a. Andreasch, *M.* 3, 85). Crystals, sl. sol. cold water, v. sol. NH_3Aq. Reduced by zinc-dust to caffeïne. Alcoholic KOH forms ethoxy-caffeïne.

BROMO-CAMPHOR *v.* CAMPHOR.

BROMO-CAMPHORIC ACID *v.* CAMPHORIC ACID.

BROMO-CAPRIC ACID *v.* BROMO-DECOIC ACID.

BROMO-CAPROIC ACID *v.* BROMO-HEXOIC ACID.

BROMO-CARBANILIC ACID *v.* PHENYL-CARBAMIC ACID.

BROMO-CARBAZOLE $C_{12}H_8BrN$. [199°]. From its acetyl derivative and alcoholic KOH. Rhombic plates, v. sol. water.

Acetyl derivative $C_{12}H_7AcBrN$. [128°]. From acetyl-carbazole and Br. Laminæ, v. sol. alcohol and boiling toluene (Ciamician a. Silber, *G.* 12, 276).

TRI-BROMO-CARBOPYRROLIC ACID *v.* TRI-BROMO-PYRROL-CARBOXYLIC ACID.

γ-BROMO-CARBOSTYRIL C_9H_6NOBr *i.e.*

$$C_6H_4\left\langle\begin{array}{l}C(Br){:}CH\\ \qquad\quad\;\,|\\ N{:}\quad\;\; C(OH)\end{array}\right.$$

. (*Py.* 1, 3)-*Bromo-oxy-quinoline.* [266°]. Formed by boiling *o*-amido-phenyl-propiolic acid with dilute HBr (Baeyer a. Bloem, *B.* 15, 2149). Prepared by the action of bromine on carbostyril-ether and saponification of the product by heating with HCl (Friedländer a. Weinberg, *B.* 15, 2682). Needles; may be sublimed. The Br is not replaced by boiling with alcoholic KOH, but requires to be fused with KOH at 200°C.

BROMO-CARVACROL $C_{10}H_{13}BrO$ *i.e.* $C_6H_2Me(OH)Br(C_3H_7)$ [1:2:3 or 5:4]. From bromo-cymidine and HNO_2. Oil (Mazzara, *G.* 16, 194).

BROMO-CHLORAL *v.* DI-CHLORO-BROMO-ALDEHYDE.

BROMO-CHLORO- *v.* CHLORO-BROMO-.

BROMO-CHLOROFORM *v.* DICHLORO-BROMO-METHANE.

BROMO-DICHROMAZIN *v.* TRI-AMIDO-PHENOL, p. 172.

BROMO-CHRYSENE *v.* CHRYSENE.

BROMO-CHRYSOQUINONE *v.* CHRYSO-QUINONE.

BROMO-CINCHONINE *v.* CINCHONINE.

BROMO-CINNAMENE *v.* BROMO-STYRENE.

DI-BROMO-CINNAMENYL-THIENYL-KETONE *v.* THIENYL-DI-BROMO-STYRYL KETONE.

α-BROMO-CINNAMIC ACID $C_9H_7BrO_2$ *i.e.* $C_6H_5.CH{:}CBr.CO_2H$ [131°].

Formation.—1. Together with *allo*-α-bromo-cinnamic acid by the action of alcoholic KOH on the di-bromide of cinnamic acid $C_6H_5.CHBr.CHBr.CO_2H$ (Glaser, *A.* 143, 325).—2. From *exo*-tri-bromo-β-phenyl-propionic acid and water at 100° (Kinnicutt a. Palmer, *Am.* 4, 26; 5, 386).

Preparation.—Dibromide of cinnamic acid (50 grms.) is dissolved in hot alcohol and mixed with the calculated quantity (2 equivalents) of potash dissolved in alcohol. The liquid is neutralised with HCl and the alcohol boiled off. The solution of the mixed potassium salts is filtered from bromo-styrene [218°]. The two acids are separated by partial precipitation with HCl, the α-acid coming down first (Barisch, *J. pr.* 128, 178).

Properties. Long needles (from water or chloroform). V. e. sol. alcohol.

Salts.—NH_4A': arborescent groups of flat needles, sl. sol. cold water.—AgA': sl. sol. water.—BaA'_2: thin rhombic laminæ. S. ·12 at 6°. Insol. alcohol.

Reactions.—1. *Sodium-amalgam* reduces it to β-phenyl-propionic acid.—2. *Alcoholic KOH* gives phenyl-propiolic acid.—3. Br gives a tri-bromo-phenyl-propionic acid [132°].—4. Both α and allo-α-bromo-cinnamic acids may be reduced by zinc-dust and glacial acetic acid to cinnamic acid, which seems to be the same in both cases (Michael, *J. pr.* [2] 35, 357).—5. Is not altered by dissolving in H_2SO_4 and pouring into water.

Methyl ether A'Me: (159°) at 14 mm. Formed by distillation of the isomeric methyl ether corresponding to the acid [120°] under ordinary atmospheric pressure (A. a. S.).

Ethyl ether A'Et: (290°); (202°) at 30 mm.; (160°) at 10 mm.; (188°) at 30 mm. V.D. = 8·715 (obs.) (Michael a. Browne, *B.* 20, 551). Formed by distillation of the isomeric ethyl-ether corresponding to the acid [120°] under ordinary atmospheric pressure (Anschütz a. Selden, *B.* 20, 1384). Prepared by passing HCl into a solution of the acid in alcohol (4 pts.) (Barisch, *loc. cit.*). By cold conc. H_2SO_4 it is converted into benzoyl-acetic ether (Michael a. Browne, *B.* 19, 1392).

Chloride: (153°) at 12 mm.; clear oily liquid. Formed by the action of PCl_5 upon salts of the acid [131°] or of its isomeride [120°].

Amide: [119°]; very thin pearly plates; sl. sol. hot water.

Anilide: [80°]; small white needles, which change into six-sided plates (A. a. S.).

Exo-Bromo-cinnamic acid $C_9H_7BrO_2$. [134°]. Formed, together with the isomeride [159°] by the addition of HBr to phenyl-propiolic acid. Long needles (from water). Thick rhombic prisms (from chloroform). V. sol. alcohol and hot benzene, sl. sol. CS_2, hot petroleum-ether and hot water.—$A'NH_4{}^{x}$: flat needles, sol. hot water, sl. sol. cold.—A'_2Ba: glistening rhombic plates; S. ·776 at 6°, m. sol. hot water. It is doubtful whether this acid is a distinct isomeride or is identical with the preceding acid; the solubility of the barium salt appears to point to the former conclusion (Michael a. Browne, *B.* 20, 550).

Allo-α-Bromo-cinnamic acid $C_6H_5.CH{:}CBr.CO_2H$. [120°]. Formed, together with α-bromo-cinnamic acid (*v. Preparation*) by boiling the dibromide of cinnamic acid with alcoholic KOH (Glaser, *A.* 143, 330). Six-sided laminæ (from water) or thick prisms (from ether). V. sol. boiling water.

Salts.—KA': deliquescent needles.—AgA'. The **ammonium salt** is deliquescent and v. sol. water (difference from α acid).

Reactions.—1. *Reactions* 1, 2, and 4 described under α-bromo-cinnamic acid are also exhibited by the allo-α- acid. *Reaction* 3 gives, however, a different tri-bromo-phenyl-propionic acid [45°–48°].—2. On dissolving in H_2SO_4 and pouring into water two products are obtained: (*a*) A substance $C_{18}H_{12}O_4$; yellow needles [above 260°], sol. alkalis, alcohol, ether and benzene. (*b*) A substance $C_{17}H_{12}Br_2O_2$; large pearly plates [above 260°], insol. alkalis, sol. phenol, nitro-benzene and aniline, insol. most other solvents, forms a crystalline molecular compound with phenol; on reduction with zinc-dust and acetic acid it gives a substance $C_{17}H_{14}O_2$ which forms colourless crystals, [127°], sol. alcohol, sl. sol. hot water (Leuckart, *B.* 15, 16).

Methyl ether A'Me: (146°) at 11 mm.; from A'Ag and MeI; by distillation at ordinary pressure it is converted into the methyl ether of the isomeric acid [131°] (Anschütz a. Selden, *B.* 20, 1383).

Ethyl ether A'Et: (174°) at 30 mm.; (177°) at 30 mm.; V.D. = 8·828 (obs.) (Michael a.

Browne, *B.* 20, 551). From A'Ag and EtI. By distillation under ordinary pressure it is converted into the ethyl ether of the isomeric acid [131°] (Anschütz a. Selden, *B.* 20, 1384).

? *β*- **Bromo-cinnamic acid**

$C_6H_5.CBr:CH.CO_2H$ (?) [159°]. Formed, together with the acid [134°], by the action of aqueous HBr upon phenyl-propiolic acid at 0°. Long flat needles (from water); or rhombic plates (from alcohol). Sl. sol. cold alcohol and benzene. By cold conc. KOH or NH_3 it is at once converted into an indifferent insoluble oil. Heating with HBr forms phenyl-acetic aldehyde and acetophenone. It combines with Br forming a tri-bromo-hydro-cinnamic acid [148°].

Salts.—NH_4A': long soluble needles.—BaA'_2aq: soluble concentric prisms.—PbA'_2: amorphous pp.—CdA'_2: concentric needles (Michael a. Browne, *B.* 19, 1378).

Ethyl ether A'Et: (151°) at 15 mm.; V.D. 8·948 (obs.) (M. a. B., *B.* 20, 551).

Bromo-cinnamic acid [153°]. This was obtained by Erlenmeyer a. Stockmeier by the addition of HBr to phenyl-propiolic acid. Aqueous Na_2CO_3 converted it into phenyl-acetylene, *a*-bromo-styrene $C_6H_5CBr:CH_2$, and phenyl-propiolic acid. Successive treatment with conc. H_2SO_4 and water gave benzoyl-acetic acid and bromo-acetophenone. Heating with HBr gave acetophenone and a little phenyl-acetic aldehyde (Erlenmeyer, *B.* 19, 1936). According to Michael a. Browne this acid is a mixture of the two acids [159°] and [134°].

o-**Bromo-cinnamic acid** [1:2]

$C_6H_4(Br)\,CH:CH.CO_2H$. *Bromo-β-phenyl-acrylic acid.* [213°]. Formed by diazotising *o*-amido-cinnamic acid and boiling the diazo-compound with HBr (Gabriel, *B.* 15, 2294). Flat colourless needles or scales. Sol. alcohol, ether and acetic acid, sl. sol. chloroform, benzene and CS_2.

m-**Bromo-cinnamic acid**

[1:3] $C_6H_4(Br).CH:CH.CO_2H$. [179°]. Formed like the preceding from *m*-amido-cinnamic acid (Gabriel, *B.* 15, 2296). Long needles. Sol. alcohol, acetic acid, hot benzene, chloroform, and CS_2.

p-**Bromo-cinnamic acid**

[1:4] $C_6H_4(Br).C_2H_2.CO_2H$. [c. 253°]. Fine needles. From *p*-amido-cinnamic acid (Gabriel, *B.* 15, 2300).

Di-bromo-cinnamic acids $C_9H_6Br_2O_2$ *i.e.* $C_6H_5.CBr:CBr.CO_2H$. Bromine unites with phenyl-propiolic acid producing di-bromo-cinnamic [139°] and allo-di-bromo-cinnamic acid [100°]. The acid [139°] is not converted into an indonaphthene derivative by conc. H_2SO_4, whereas the acid [100°] forms $C_6H_4\left\langle\begin{matrix}CO\\C_2Br_2\end{matrix}\right\rangle$ [123°] (whence hydroxylamine forms an oxim [195°], and aniline forms an anilide [17?°]) (W. Roser, *B.* 20, 1273, 1576).

a-**BROMO-CINNAMIC ALDEHYDE** C_9H_7BrO *i.e.* $C_6H_5.CH:CBr.CHO$ [73°]. Formed from cinnamic-aldehyde-di-bromide by splitting off HBr (Zincke a. Hagen, *B.* 17, 1815). Thick tables or large monoclinic prisms. CrO_3 gives bromo-cinnamic acid [131°].

Phenyl-hydrazide

$C_6H_4.C_2HBr.CH:N_2HC_6H_5$ [130°], glistening yellow plates

BROMO- CITRACONIC ACID $C_5H_5BrO_4$ *i.e.* $CH_3.C(CO_2H):CBr.CO_2H$(?).

Formation.—1. From its anhydride by boiling with water.—2. From *citra*-di-bromo-pyrotartaric acid, water, and Ag_2O in presence of a trace of HCl: $C_5H_6Br_2O_4 = HBr + C_5H_5BrO_4$ (Bourgoin, *C. R.* 88, 342; 89, 418; *A. Ch.* [5] 19, 285).

Properties.—Very unstable, giving off water even over H_2SO_4 and changing to the anhydride.

Reactions.—1. *Sodium amalgam* forms pyrotartaric acid.—2. Boiling KOH forms a syrupy dibasic acid $C_5H_4O_4$.—3. *Evaporation* of its solution produces bromo-citraconic anhydride and, at a low temperature, the acid $C_5H_4O_5$, but at a high temperature 'bromo citronic acid' $C_4H_5BrO_2$ (B.).—4. The aqueous solution treated with the equivalent of *aniline* gives a crystalline pp. of the acid aniline salt. [121°]. Standing under water for a few hours, or heating the aqueous solution for a minute, converts it into the phenylimide $\begin{matrix}C(CH_3)-CO\\ \| \\ CBr-\ \ CO\end{matrix}\!\!>NPh$. [145°]. This forms stellate groups of prismatic needles. Sl. sol. hot water; v. sol. hot alcohol; insol. dilute HCl (Michael, *Am.* 9, 180). An intermediate body is the acid anilide $C_3H_4Br(CO_2H).CONPhH$ [212°] (Michael, *B.* 19, 1373).

Salts.—$(NH_4)_2A''$.—K_2A''.—$CaA''2aq$.—$CaA''1\frac{1}{2}aq$.—$BaA''aq$.—Ag_2A''. Decomposed by water at 130° giving off CO_2, and allylene.

Anhydride $C_5H_3BrO_3$. [100°]. (220°). S.G. $\frac{??}{4}$ 1·935 (Kekulé, *A. Suppl.* 1, 130; 2, 97; Lagermark, *Z.* 1870, 299; Fittig a. Krusemark, *A.* 206, 19; Bourgoin, *Bl.* [2] 31, 252; 32, 388). *Formation.*—1. From citraconic anhydride and Br at 140°. 2. By distilling *citra*-dibromo-tartaric acid.—3. From pyrotartaric acid, Br, and water at 120°. *Properties.* Laminæ (from CS_2); sl. sol. cold water, v. e. sol. alcohol and ether; volatile with steam.

Imide $C_5H_3BrO_2NH$. [c. 181°]. From pyrotartrimide or citraconimide and Br at 150° (Mendini, *G.* 15, 182). Laminæ; may be sublimed.—$C_5H_3BrO_2NAg$.

Di-bromo-citraconic acid. *Imide.*

$C_5H_2Br_2O_2NH$. [144°]. From pyrotartrimide or citraconimide and Br (M.). Laminæ; may be sublimed.—$C_5H_2Br_2O_2NAg$.

BROMO-CODEÏNE *v.* CODEÏNE.

DI-BROMO-COLLIDINE *v.* DI-BROMO-TRI-METHYL-PYRIDINE.

BROMO- COMPOUNDS. Bromine unites directly with most unsaturated compounds, but there are some cases in which it does not combine with them in the cold, *e.g.* fumaric, mesaconic, teraconic, terebilenic, aconic, *o*- and *p*- coumaric, and (*β*)-hydropiperic acids (*cf.* Fittig, *A.* 22?, 29). Aromatic compounds combine with great difficulty with bromine, but when reduced to their di- or tetrahydrides they take up bromine as readily as the ordinary unsaturated compounds. Bromine displaces hydrogen in saturated compounds, the displaced hydrogen being given off as HBr; this reaction usually requires the aid of heat: the substance is generally heated with bromine and a little water in a sealed tube.

Hydroxyl may be displaced by bromine by treatment with HBr or PBr_3; instead of PBr_3

red phosphorus and bromine may be used, one of the two being added gradually.

Chlorine may be displaced by bromine by treatment with the bromide of K, Mg, Ca, Sr, Ba, Al, Mn, or Co (Köhnlein, *A.* 225, 194). $CdBr_2$, $SbBr_3$ and $AsBr_3$ sometimes act similarly; thus $AsBr_3$ at 115° completely converts chloro-acetic acid and benzyl chloride into bromo-acetic acid and benzyl bromide respectively.

Iodine may be displaced by bromine by means of the bromides of Cu, Ag, Hg, Sn, Pb, As, and Sb. $BiBr_3$ at 160° only partially converts EtI into EtBr. Bromine itself can displace iodine (R. Meyer, *J. pr.* [2] 34, 104).

Amidogen may be displaced by bromine by using the diazo- reactions (p. 399). In aromatic compounds it is sufficient to add HNO_2 to a hot solution of the amine in HBr (Losanitsch, *B.* 18, 39, *v. also* AMINES).

Carriers.—The displacement of hydrogen by Br is assisted by the presence of carriers which first combine with the bromine, and then pass it on to the organic body. The most suitable carriers for bromine are: iodine; Al_2Br_6 (Gustavson, *B.* 10, 971) for benzene and homologues; amorphous P for fatty acids (Hell a. Gantter, *B.* 14, 891), $SbBr_3$, Fe_2Br_6, $FeBr_2$, and, better still, $FeCl_3$ (Scheufelen, *A.* 231, 154; *cf.* Willgerodt, *J. pr.* [2] 34, 264).

Bromination of organic acids. The following is a very convenient method, which depends upon the fact that the acid bromides and anhydrides are much more easily brominated than the acids themselves. The acid is mixed with amorphous phosphorus in quantity sufficient to convert it into the bromide or anhydride, and the corresponding quantity of bromine added together with the extra amount required for bromination. The mixture is heated to 100° till decolourised, when the reaction is complete (Hell, *B.* 14, 891). The bromination of fatty acids may also be readily effected by boiling their chlorides with Br and CS_2 (Michael, *J. pr.* [2] 35, 92). Alkalis or water acting upon α-bromo- acids usually produce α-oxy- acids, with β-bromo- acids they form unsaturated acids, while γ-chloro- acids become lactones (Fittig, *A.* 195, 169; Erlenmeyer, *B.* 14, 1318; 15, 49).

Bromination of aromatic hydrocarbons. Bromine in presence of a carrier enters the benzene nucleus; bromine alone, or in presence of too little iodine, enters the side-chains of boiling hydrocarbons. Sunlight promotes substitution in the side-chains (Schramm, *B.* 17, 2922; 18, 350, 1272; 19, 212).

Bromination of aromatic amines. Bromine goes first into a position *p* to the NH_2, and then into the *o-* positions, but not into a *m-* position (Nevile a. Winther, *B.* 13, 962; *v.* also AROMATIC COMPOUNDS, p. 299).

Stability of bromo- compounds. Bromo- compounds are less stable than the corresponding chloro- compounds; thus bromo-acetic and bromo-propionic acids may be converted by reduced silver into succinic and adipic acids respectively, in this they differ from the corresponding chloro- but resemble the iodo- acids. The relative stability of the alkyl bromides depends upon the reagents attacking them; thus Zn and H_2SO_4 reduces iso-propyl bromide more quickly than propyl bromide, the order being isopropyl, isoamyl, butyl, propyl, ethyl; on the other hand, alcoholic NaOH attacks propyl bromide more vigorously than isopropyl bromide, the order being ethyl, propyl, isoamyl, butyl, isopropyl (Remsen a. Hillyer, *Am.* 8, 251).

Other characteristics of bromo- compounds may be inferred from the article on CHLORO-COMPOUNDS; the bromo- compounds resemble the chloro- compounds in almost every respect.

BROMO-CONIINE *v.* CONIINE.

BROMO - COUMARIC ACID $C_9H_7BrO_3$ *Bromo-o-oxy-cinnamic acid. Methyl derivative* $MeO.C_6H_4.C_2HBr.CO_2H$. [171°]. S. (CS_2) ·32 at 14°. From the methyl derivative of α- or β- di-bromo-melilotic acid $MeO.C_6H_4.C_2H_2Br_2.CO_2H$ and aqueous KOH (Perkin, *C. J.* 39, 422). Small prisms (from CS_2): sl. sol. boiling water, v. sol. alcohol. Boiling dilute KOH forms the methyl derivative of cumarilic acid $MeO.C_6H_4.C_2.CO_2H$.

Ethyl derivative $EtO.C_6H_4.C_2HBr.CO_2H$ [164°]. From $EtO.C_6H_4.C_2H_2Br_2.CO_2Et$ and cold alcoholic KOH (P.). Flat prisms; sl. sol. boiling water, m. sol. CS_2, v. sol. alcohol.

(α)-BROMO-COUMARIN $C_9H_5BrO_2$. [110°] From coumarin dibromide and alcoholic KOH (Perkin, *C. J.* 23, 368). Prisms; converted by alcoholic KOH into cumarilic acid.

(β) - Bromo - coumarin $C_9H_5BrO_2$. [160°] From sodium bromo-*o*-oxy-benzoic aldehyde and Ac_2O. Rhombic prisms (from alcohol) (Perkin, *C. J.* 24, 37).

(α)-Di-bromo-coumarin $C_9H_4Br_2O_2$. [183°] From coumarin, Br, and I (P.). Needles; alcoholic KOH forms bromo-cumarilic acid.

(β)-Di-bromo-coumarin $C_9H_4Br_2O_2$. [176°] From sodium di-bromo-*o*-oxy-benzoic aldehyde and Ac_2O. Needles (P.).

BROMO-*o*-CRESOL $C_6H_3MeBr(OH)$ [1:3?:6] [89°]. From bromo-*o*-toluidine (Wroblewsky *A.* 168, 165). Golden needles; v. sl. sol. water; the aqueous solution is turned green by Fe_2Cl_6.—KC_7H_6BrO aq: red scales.

Bromo - *m* - cresol $C_6H_3MeBr(OH)$ [1:3:5] [57°]. From *s*-bromo-toluidine by diazo- reaction (Nevile a. Winther, *C. J.* 41, 421).

Bromo - *p* - cresol $C_6H_3(CH_3)Br.OH$ [1:3:4] (214°). S.G. $\frac{25}{25}$ = 1·5468. Liquid. Formed by the action of dry bromine upon sodium-*p*-cresol

Methyl ether $C_6H_3MeBr(OMe)$: (226°); S.G. $\frac{25}{25}$ 1·418; liquid (Schall a. Dralle, *B.* 17 2530).

Di - bromo - *o* - cresol $C_6H_2MeBr_2(OH)$. [57°] From *o*-cresol and Br. Volatile with steam (Werner, *Bl.* [2] 46, 278).

Di-bromo-*p*-cresol $C_6H_2(CH_3)Br_2.OH$ [1:3:5:4] [49°]. Large crystals. V. sol. alcohol, v. sl. sol. water. Excess of Br forms $C_6H_2Br_3(OBr)$ (W.).

Benzoyl derivative $C_6H_2MeBr_2(OBz)$ [91°], white needles (Schall a. Dralle, *B.* 17, 2532; Werner, *Bl.* [2] 46, 278).

Tri-bromo-*m*-cresol $C_6HMeBr_3(OH)$. [82°] From *m*-cresol (W.). Needles (from alcohol).

Tetra-bromo-*p*-cresol $C_6Br_4Me(OH)$. [109°] From *p*-cresol (Baumann a. Brieger, *B.* 12, 804). Plates; slowly decomposed by cold bromine-water into CO_2 and tri-bromo-phenol.

BROMO-CRESOL SULPHONIC ACID $C_6H_2MeBr(OH)(SO_3H)$ [1:2 or 6:5?:3]. From *o*-bromo-toluene by sulphonation, nitration, re-

duction, and diazotisation (Schäfer, *A.* 174, 361).—BaA'_2 4½aq.—BaA'_2 3aq.—PbA'_2 2aq.

Bromo-cresol sulphonic acid $C_6H_2MeBr(OH)(SO_3H)$ [1:4:5?:3]. From (3,1,2)-bromo-toluene sulphonic acid by nitration, reduction, and diazotisation (S.).—BaA'_2 3aq.

Bromo-cresol sulphonic acid $C_6H_2MeBr(OH)(SO_3H)$ [1:4:?:2]. From (4,1,2)-bromo-toluene sulphonic acid in a similar way.—BaA'_2 aq.

Di-bromo-cresol sulphonic acid $C_6HMeBr_2(OH)(SO_3H)$. From (2,1,4)-amido-toluene sulphonic acid and Br (Hayduck, *A.* 174, 353).—KA'aq. BaA'_2 8½aq.

a-BROMO-CROTONIC ACID $C_4H_5BrO_2$ *i.e.* $CH_3.CH:CBr.CO_2H$. [106·5°].

Formation.—1. From aa-di-bromo-*n*-butyric acid and alcoholic KOH, NH_3, baryta-water, or Ag_2CO_3 (Michael a. Norton, *Am.* 2, 15; Erlenmeyer a. Müller, *B.* 15, 49).—2. From aβ-di-bromo-butyric ether and alcoholic KOH (Michael a. Browne, *Am.* 9, 280).—3. Together with bromo-pyrotartaric acid by the action of bromine on propane tri-carboxylic acid (Bischoff a. Guthzeit, *B.* 14, 616).

Properties.—Long needles (from water); needles (from ligroïn); m. sol. cold, v. sol. hot, water.—AgA': white needles, quickly affected by light.—BaA'_2 2aq.

Allo-a-Bromo-crotonic acid $CH_3.CH:CBr.CO_2H$. [90°] (K.); [92°] (M. a. N.). From aβ-di-bromo-butyric acid (dibromide of crotonic acid) by treatment with alcoholic KOH (Michael a. Norton, *Am.* 2, 15) or NaOHAq (C. Kolbe, *J. pr.* [2] 25, 394).

Properties.—Long needles (from water); needles (from ligroïn); m. sol. hot water.—AgA': needles, little affected by light.—BaA'_2 3½aq.—CaA'_2 3aq.

β-Bromo-crotonic acid $CH_3.CBr:CH.CO_2H$. [95°]. From tetrolic acid and conc. HBrAq at 0° (Michael a. Browne, *Am.* 9, 277; *J. pr.* [2] 35, 258). Flat needles (from water); feathery groups of tough needles (from ligroïn); sl. sol. cold water, m. sol. hot water.—AgA': amorphous, readily affected by light.—BaA'_2 aq.—KA'.

aβ-Di-bromo-crotonic acid $CH_3.CBr:CBr.CO_2H$. [96°]. From tetrolic acid and Br (Pinner, *B.* 14, 1081).—Boiling with Ag_2O gives $(C_3H_3Br)_x$. [116°].

BROMO-CUMALIC ACID $C_5H_2BrO_2(CO_2H)$. [176°]. Formed by the action of bromine on cumalic acid in acetic acid solution (Pechmann a. Welsh, *B.* 17, 2396). Colourless glistening needles. Can be distilled in small quantities. V. sol. alcohol, ether, acetic acid, and chloroform, more sparingly in benzene, insol. ligroin.

Methyl ether A'Me: [134°], prismatic needles, sol. alcohol and benzene, sl. sol. ether, insol. water. Aqueous NH_3 converts it into the methyl ether of brom-oxy-nicotinic acid.

o-BROMO-*n*-CUMENE $C_9H_{11}Br$ *i.e.* C_6H_4BrPr [1:2]. *Bromo-n-propyl-benzene.* (222 i. V.). A mixture of this body with the *p*- isomeride is formed by the action of Br on propyl-benzene in the dark or on ethyl-benzene mixed with I in diffused daylight (Schramm, *B.* 18, 1274). $KMnO_4$ gives *o*-bromo-benzoic acid.

p-Bromo-*n*-cumene C_6H_4BrPr [1:4]. (220° cor.) From C_6H_5Pr and Br at 0° in presence of I (Meyer a. Müller, *B.* 15, 698; R. Meyer, *J. pr.* [2] 34, 101). HNO_3 (S.G. 1·2) forms *p*-bromo-benzoic acid.

β-Bromo-*n*-cumene $C_6H_5.CHBr.CH_2.CH_3$. Formed in the cold by the action of bromine (1 mol.) upon *n*-cumene in direct sunshine. By further bromination in sunlight it gives ββ-di-bromo-*n*-cumene $C_6H_5.CBr_2.CH_2.CH_3$, but in the dark at 100° it yields aβ-di-bromo-*n*-cumene $C_6H_5.CHBr.CHBr.CH_3$ (Schramm, *B.* 18, 1275).

aβ-Di-bromo-*n*-cumene $C_6H_5.CHBr.CHBr.CH_3$. From allyl-benzene (*q.v.*) and bromine (Rügheimer, *A.* 172, 131; Radziszewski, *C. R.* 78, 1153; Perkin, *C. J.* 32, 668). From *n*-cumene and bromine at 160° (Wispek a. Zuber, *A.* 218, 381; *cf.* S. *supra*). Silky needles (from alcohol).

ββ-Di-bromo-*n*-cumene $C_6H_5.CBr_2.CH_2.CH_3$. *Phenyl-ethyl-ketone-di-bromide.* Formed in the cold by the action of bromine (2 mols.) upon *n*-cumene exposed to direct sunshine (Schramm *B.* 18, 1275).

ωaβ-Tri-bromo-*n*-cumene $C_6H_5.CHBr.CHBr.CH_2Br$. *Stycerin tri-bromhydrin.* [124°]. From cinnamyl bromide and Br, or by the action of HBr on the dibromide of cinnamyl alcohol (Grimaux, *Bl.* 20, 120).

Tetra-bromo-*n*-cumene $C_9H_8Br_4$. Liquid (Fittig, *A.* 149, 327).

o-Bromo-cumene C_6H_4BrPr [1:2]. *Bromo-isopropyl-benzene.* (206° cor.) at 740 mm. From isopropyl-phenol and PBr_5 (Fileti, *G.* 16, 131).

p-Bromo-cumene C_6H_4BrPr [1:4]. (217°). S.G. $\frac{15}{15}$ 1·3014. Prepared by brominating cumene at 0° in presence of I (Jacobsen, *B.* 12, 430). With benzene, Na, and CO_2 it gives cuminic acid (R. Meyer, *J. pr.* [2] 34, 93).

Penta-bromo-cumene $C_9H_7Br_5$. [97°]. From cumene and Br (Meusel, *Z.* 1867, 322; Fittig, *A.* 149, 326). Needles; sl. sol. cold alcohol.

Bromo-ψ-cumene $C_6H_2(CH_3)_3Br$ [1:2:4:5]. [73°]. (227°). White plates.

Formation.—1. By the action of cuprous bromide upon diazo-pseudo-cumene (Haller, *B.* 18, 93).—2. By the action of bromine (1 mol.) in the dark upon pseudo-cumene; the yield is 60 p.c. (Beilstein, *A.* 137, 323; Fittig, *A.* 139, 188; 145, 138; Schramm, *B.* 19, 216; Süssenguth, *A.* 215, 243). 3. By the action of bromine upon an aqueous solution of pseudo-cumene-sulphonic acid (1:2:4:5) 76 p.c. is converted into bromo-ψ-cumene, the remainder forming bromo-ψ-cumene sulphonic acid $C_6HMe_3Br(SO_3H)$ [1:2:4:3:5] (Kelbe a. Pathe, *B.* 19, 1547).

Bromo-ψ-cumene $C_6H_2Me_3Br$ [1:2:4:3]. (226°-229°). Colourless oil. Formed by the hydrolysis of the sulphonic acid $C_6HMe_3Br(SO_3H)$ [1:2:4:3:5] by means of superheated steam at 200°-210°. By MeI and Na it yields *c*-tetra-methyl-benzene (Kelbe a. Pathe, *B.* 19, 1551).

Bromo-ψ-cumene $C_6H_2Me_3Br$ [1:2:4:6] (237°). Liquid; still fluid at -15°. Obtained by hydrolysis of the sulphonic acid (1:3:4:5:2). By sulphonation it is reconverted into the same sulphonic acid (Jacobsen, *B.* 19, 1223).

ω-Bromo-ψ-cumene $C_6H_3(CH_3)_2.CH_2Cl$. *Pseudo-cumyl bromide.* Liquid. Decomposes on distillation. Formed by the action in direct sunshine of 1 mol. of bromine upon 1 mol. pseudo-cumene (Schramm, *B.* 19, 217).

Di-bromo-ψ-cumene $C_6HMe_3Br_2$ [1:2:4:5:6]. [64°]. (294°). Formed by the action of 1 mol. of bromine upon 1 mol. mono-bromo-pseudo-

cumene by gaslight, or in the dark (Schramm, B. 19, 216; Jacobsen, B. 19, 1220). Long flat needles, v. sol. alcohol.

ω_1-ω_2-Di-bromo-ψ-cumene $C_6H_3(CH_3)(CH_2Br)_2$ [1:2:4]. *Pseudo-cumylene bromide.* [97°]. Flat glistening needles (from petroleum-ether). V. sol. alcohol and benzene. Formed by the action of 2 mols. of bromine upon 1 mol. pseudo-cumene *in direct sunshine* (Schramm, *B.* 19, 218; Hjelt a. Gadd, *B.* 19, 867).

Tri-bromo-ψ-cumene $C_6Me_3Br_3$ [1:2:4:3:5:6]. [226°] or [233° cor.]. V. sol. hot toluene, sl. sol. alcohol. Formed by the action of Br (3 mols.) in the dark upon ψ-cumene (1 mol.) (Fittig a. Laubinger, *A.* 151, 264; Schramm, *B.* 19, 217; Jacobsen, *B.* 19, 1222).

BROMO-ψ-CUMENE-SULPHONIC ACID $C_6HMe_3Br(SO_3H)$ [1:2:4:5:6]. [c. 121°]. Formed by dissolving bromo-ψ-cumene [73°] in warm slightly fuming H_2SO_4. Needles (containing 2aq). By treating the Na salt with zinc-dust and aqueous NH_3 it is debrominated with production of (1,2,4,6)-pseudo-cumene-sulphonic acid.

Salts.—A'Na aq.—A'_2Ca 3aq.—CuA'_2 4aq.—BaA'_2 ½aq.—KA' aq.

Amide $C_6HMe_3Br(SO_2NH_2)$: [185°]; small needles, v. sol. alcohol, nearly insol. water (Jacobsen, *B.* 19, 1218; Kelbe a. Pathe, *B.* 19, 1553).

Bromo-ψ-cumene-sulphonic acid $C_6HMe_3Br(SO_3H)$ [1:2:4:6:3]. Formed, together with the di-bromo- acid, by the action of $ClSO_3H$ upon di-bromo-ψ-cumene.—NaA' ½aq.

Amide $C_6HMe_3Br(SO_2NH_2)$: [158°]; thin needles (Jacobsen, *B.* 19, 1223).

Bromo-ψ-cumene-sulphonic acid $C_6HMe_3Br(SO_3H)$ [1:2:4:3:5]. [116°]. Colourless needles. Formed by the action of bromine upon an aqueous solution of pseudo-cumene-sulphonic acid [1:2:4:5]; 76 p.c. of the pseudo-cumene-sulphonic acid is converted into bromo-pseudo-cumene [73°], the remainder yielding the bromo-sulphonic acid. It is also formed by sulphonation of bromo-pseudo-cumene [1:2:4:3]. The latter body is formed by the action of superheated steam upon it at 200°-210°.

Salts.—NaA'aq.—KA' aq.—AgA' aq.—BaA'_2 aq.—PbA'_2 3aq.

Amide $C_6HMe_3Br(SO_2NH_2)$: [188°]; thin needles (Helbe a. Pathe, *B.* 19, 1547).

Di-bromo-ψ-cumene-sulphonic acid $C_6Me_3Br_2(SO_3H)$ [1:2:4:5:6:3]. Obtained by sulphonation of di-bromo-pseudo-cymene with sulphuric chlorhydrin.

Salts.—NaA'.—NaA' aq.—BaA'_2.

Amide $C_6Me_3Br_2(SO_2NH_2)$: [above 250°]; plates (Jacobsen, *B.* 19, 1222).

BROMO-ψ-CUMENOL $C_6HMe_3Br.OH$ [1:2:4:3:5]. [35°]. Formed by bromination of pseudo-cumenol in cold acetic acid. Slender yellow needles. Insol. water, v. sol. other solvents (Reuter, *B.* 11, 29; Auwers, *B.* 18, 2657).

Bromo-iso-cumenol $C_6H_3PrBr(OH)$ [2:4:1]. [49°]. *Bromo-isopropyl-phenol.* From o-iso-propyl-phenol (o-isocumenol) and Br (Fileti, *G.* 16, 117). Decomposes at 250°.

Methyl ether $C_6H_3PrBr(OMe)$. (250°).

Di-bromo-ψ-cumenol $C_6Me_3Br_2.OH$ [1:2:4:3:6:5]. [149°]. Formed by bromination of pseudo-cumenol dissolved in a small quantity of acetic acid. Long colourless prisms or needles. Insol. water, m. sol. alcohol, acetic acid, and benzene, v. sol. ether.

Methyl ether $C_6Me_3Br_2.OMe$: [96°]. Formed by methylation of the above or by bromination of pseudo-cumenol-methyl ether. White needles. Insol. water, v. sol. other solvents (Auwers, *B.* 18, 2657).

Di-bromo-ψ-cumenol $C_6Me_3Br_2OH$ [1:2:4:3:5:6]. [152°]. From $C_6HMe_3Br_2$ [1:3:4:2:6] (Edler, *B.* 18, 630; Jacobsen, *B.* 19, 1220).

Di-bromo-iso-cumenol $C_6H_2PrBr_2(OH)$ [2:4:6:1]. From o-iso-cumenol and Br (Fileti). Liquid.

Methyl ether $C_6H_2PrBr_2(OMe)$. (279°). HNO_3 forms a nitro-derivative $C_6H_2PrBr(NO_2)(OH)$ [2:4:6:1]. [33°].

BROMO-CUMINIC ACID $C_{10}H_{11}BrO_2$ *i.e.* $C_6H_3Br(C_3H_7)CO_2H$. [151°]. *Bromo-propyl-benzoic acid.* From Br and cuminic acid or silver cuminate (Naquet a. Luginin, *Z.* 1866, 333; Gerichten, *B.* 11, 1719). From bromo-cymene and HNO_3 (Fileti a. Crosa, *G.* 16, 296).

Exo-bromo-cuminic acid $C_3H_6Br.C_6H_4.CO_2H$. From Br and cuminic acid at 120° (Czumpelik, *B.* 3, 478).

BROMO-CUMYL-BUTYRIC ACID $C_{13}H_{17}BrO_2$ *i.e.* $C_6H_4Pr.C_2H_4.CHBr.CO_2H$. [150°]. From cumenyl-crotonic acid and HBr. Prisms. Decomposed by Na_2CO_3 giving allyl-isopropyl-benzene (Perkin, *C. J.* 32, 662).

BROMO-CUMYL-PROPIONIC ACID $C_{12}H_{15}BrO_2$ *i.e.* $C_6H_4Pr.CH_2.CHBr.CO_2H$. [87°]. From cumyl-acrylic acid and HBr (Perkin, *C. J.* 32, 661). Resolved by boiling water into HBr and cumyl-acrylic acid. Na_2CO_3Aq forms vinyl-isopropyl-benzene.

Di-bromo-cumyl-propionic acid $C_6H_4Pr.CHBr.CHBr.CO_2H$. [190°]. From cumyl-acrylic acid and Br (Widman, *B.* 19, 258).

BROMO-CUMYL-VALERIC ACID $C_{14}H_{19}BrO_2$ *i.e.* $C_6H_4Pr.C_3H_6.CHBr.CO_2H$. From cumenyl-angelic acid and HBr. Prisms. Na_2CO_3Aq gives isopropyl-butenyl-benzene (Perkin, *C. J.* 32, 663).

BROMO-CYANO-BENZENE *v. Nitrile of* BROMO-BENZOIC ACID.

BROMO-*p*-CYMENE $C_{10}H_{13}Br$ *i.e.* $C_6H_3(CH_3)(C_3H_7)Br$ [1:4:2]. *Bromo-p-methyl-n-propyl-benzene.* (234° i.V.). S.G. $\frac{17.5}{}$ 1·27.

Formation.—1. From cymene and Br (Landolph, *B.* 5, 267).—2. Together with bromo-*p*-cymene-sulphonic acid $C_6H_2MePrBr(SO_3H)$ [1:4:5:2] by the action of bromine upon an aqueous solution of *p*-cymene-sulphonic acid (Kelbe a. Koschitzsky, *B.* 19, 1730).—3. The same or the following bromo-cymene is formed by hydrolysis of bromo-*p*-cymene-sulphonic acid $C_6H_2MePrBr(SO_3H)$ [1:4:5or6:2] (K. a. K.).

Bromo-*p*-cymene $C_6H_3(CH_3)(C_3H_7)Br$ [1:4:3]. (232°). From thymol and PBr_5 (Fileti a. Crosa, *G.* 16, 287). Formed also by the action of bromine upon an aqueous solution of *p*-cymene-sulphonic acid (Me:Pr:SO_3H = 1:4:3) (Claus a. Christ, *B.* 19, 2165, *v. supra*).

Di-bromo-*p*-cymene $C_6H_2MeBr_2Pr$. (272°). S.G. $\frac{15}{}$ 1·596 (Claus a. Wimmel, *B.* 13, 903).

(α)-Bromo-*m*-isocymene $C_6H_3MePrBr$ [1:3:6]. (225° cor.). Formed, together with bromo-iso-cymene sulphonic acid, by the action of bromine on *m*-isocymene sulphonic acid (Kelbe, *A.* 210,

46; 235, 281). Oxidised by dilute HNO_3 to bromo-toluic acid [210°].

(β)-Bromo-isocymene $C_6H_3Me(Pr)Br$ [1:3:4]. (224°). Got by distilling $C_6H_2Me(Pr)Br(SO_3K)$ [1:3:4:6] with superheated steam (Kelbe a. Czarnomski, *A.* 235, 293). Dilute HNO_3 oxidises it to bromo-toluic acid $C_6H_3MeBrCO_2H$ [1:4:3] [153°].

Di-bromo-*m*-isocymene $C_{10}H_{12}Br_2$. (273° uncor.). Obtained by brominating (α)-bromo-*m*-isocymene sulphonic acid (Kelbe a. Czarnomski, *A.* 235, 281). Converted by fuming HNO_3 into nitro-bromo-iso-cymene $C_{10}H_{11}(NO_2)Br$ [83°].

Bromo-*p*-cymene-sulphonic acid $C_6H_2MePrBr(SO_3H)$ [1:4:5or6:2]. *Bromo-p-methyl-n-propyl-benzene sulphonic acid.* Formed, together with bromo-*p*-cymene $C_6H_3MePrBr$ [1:4:2], by the action of bromine upon *p*-cymene-sulphonic acid $C_6H_3MePr(SO_3H)$ [1:4:2] in aqueous solution at 40°-50° (Kelbe a. Koschitzky, *B.* 19, 1730). Formed also from cymidine by sulphonation and diazotisation (Widman, *B.* 19, 248). Sodium amalgam reduces it to *n*-cymene sulphonic acid.

Salts. KA'aq. BaA'_2 2½aq. S. 1 at 17°.— BaA'_2 1½aq.—CuA'_2 12aq.

Amide $C_6H_2MePrBr(SO_2NH_2)$: [152°].

Bromo-*p*-cymene-sulphonic acid $C_6H_2MePrBr(SO_3H)$ [1:4:2:5]. Formed by sulphonation of bromo-*p*-cymene (1:4:2) with H_2SO_4 (Kelbe a. Koschitzsky, *B.* 19, 1732; Claus a. Christ, *B.* 19, 2163; Remsen a. Day, *Am.* 5, 151), or $ClSO_3H$ (Paterno a. Canzoneri, *G.* 11, 126). Long needles containing 3aq [c. 60°]. By zinc-dust and NH_3 it is easily debrominated to *p*-cymene-sulphonic acid (1:4:5)?.

Salts. KA'3aq.—PbA'_2. S. 2·1 at 30°.— AgA'.—CaA'_2 8aq. NaA'4½aq (R. a. D.).— ZnA'_2 8aq (R. a. D.).—MgA'_2 9½aq (R. a. D.).— CaA'_2 9½aq (R. a. D.).—CaA'_2 6aq.—BaA'_2 9½aq (R. a. D.). BaA'_2 5aq. S. 1·37 at 27°.—CuA'_2 8aq.

Amide $C_6H_2MePrBr(SO_2NH_2)$: [188°] (K. a. K.) [195°] (C. a. C.).

Chloride $C_6H_2MePrBrSO_2Cl$ [82°].

Bromo-*p*-cymene-sulphonic acid $C_6H_2(CH_3)(C_3H_7)Br(SO_3H)$ [1:4:5:3]. [180° uncor.]. Formed by bromination of an aqueous solution of *p*-cymene-sulphonic acid $C_6H_3MePr(SO_3H)$ [1:4:3]. Glistening colourless plates (Claus a. Christ, *B.* 19, 2166).

(α)-Bromo-iso-cymene sulphonic acid $C_6H_2Me(Pr)Br(SO_3H)$ [1:3:6:4]. [65°] and [126°]. From (α)-bromo-iso-cymene by sulphonation, or from (β)-isocymene sulphonic acid by bromination (Kelbe a. Czarnomski, *A.* 235, 277). Needles containing 3aq (from water). After a week's exposure over H_2SO_4 it melts at 126°. Salts.— BaA'_2 7aq.—CuA'_2 7aq.—KA'aq.—NaA'2aq.

Amide $C_{10}H_{12}Br.SO_2NH_2$ [171°].

(β)-bromo-*m*-iso-cymene sulphonic acid $C_{10}H_{12}Br.SO_3H$ *i.e.* $C_6H_2Me(C_3H_7)Br(SO_3H)$ [1:3:4:6]. [109°]. Formed by bromination of *m*-isocymene sulphonic acid (Kelbe a. Czarnomski, *A.* 235, 272). Salts.—PbA'_2 aq.— BaA'_2.—CuA'_2 4aq.—KA'aq.

Amide.—$C_{10}H_{12}Br.SO_2NH_2$ [162°].

BROMO-CYMENOL $C_6H_2MePrBr(OH)$ [1:4:3:2or6]. From amido-cymenol by the diazo-reaction. Oil (Mazzara, *G.* 16, 191).

Tri-bromo-cymenol $C_6Me(C_3H_7)Br_3(OH)$ [2:4:1]. [222°]. Glistening golden plates. Formed by shaking an aqueous solution of cymenol with a solution of bromine in HBr (Jesurun, *B.* 19, 1414).

BROMO-CYMIDINE $C_6H_2MeBr(C_3H_7).NH_2$ From bromo-nitro-cymene. Liquid (Mazzara, *G.* 16, 193).

BROMO-DECANE *v.* DECYL BROMIDE.

Di-bromo-decane $C_{10}H_{20}Br_2$. *Decylene bromide.* Oil. From petroleum decylene (Reboul a. Truchot, *A.* 144, 248).

*Di-bromo-decane $C_{10}H_{20}Br_2$. *Diamylene bromide.* From diamylene and Br (Bauer, *A.* 135, 344). Liquid. Alcoholic KOH gives rutylene $C_{10}H_{18}$ (150°).

Tri-bromo-decane $C_{10}H_{19}Br_3$. Oil. From diamylene and Br (Walz, *Z.* 1868, 315). Decomposes at 100°.

Tetra-bromo-decane $C_{10}H_{18}Br_4$. *Menthene tetrabromide.* From menthene and Br (Beckett a. Wright, *Report of British Ass.* 1875, ii. 38). Oil, split up by distillation into HBr and cymene.

Tetra-bromo-decane $C_{10}H_{18}Br_4$. *Decenylene tetra bromide.* From decinene (165°) and Br. Oil (Reboul a. Truchot, *A.* 144, 249).

Tetra-bromo-decane $C_{10}H_{18}Br_4$. From allyl-propylidene propyl-methane (158°) and Br (Reformatsky, *J. pr.* [2] 27, 389).

DI-BROMO-DECINENES $C_{10}H_{17}Br$. Described as hydrobromides of terpenes. *V. also* BORNYL BROMIDE.

Di-bromo-decinene $C_{10}H_{16}Br_2$. From di-amylene and Br, p. 211.

Tetra-bromo-decinene $C_{10}H_{14}Br_4$. *Di-bromo-camphilidene dibromide* [160°-164°]. From camphor and PCl_3Br_2 (De la Royère, *Bl.* [2] 38, 579). Unctuous tables.

γ-BROMO-DECOIC ACID $C_{10}H_{19}BrO_2$ *i.e.* $C_6H_{13}.CHBr.CH_2.CH_2.CO_2H$. From decenoic acid (*q. v.*) and HBr (Schneegans, *A.* 227, 92). Heavy oil. Na_2CO_3 removes HBr forming the lactone of oxydecoic acid.

Di-bromo-decoic acid $C_{10}H_{18}Br_2O_2$. *Di-bromo-capric acid.* [135°]. From decenoic ('amydecylenic') acid and Br (Hall a. Schoop, *B.* 12, 194). Monoclinic prisms (from benzene).

DI-BROMO-DECYL ALCOHOL $C_{10}H_{20}Br_2O$. Oil. From allyl-di-isopropyl-carbinol and Br (Lebedinsky, *J. pr.* [2] 23, 22).

BROMO-DECYLENE $C_{10}H_{19}Br$. (215°). S.G. $\frac{15}{}$ 1·109. Oil. From decylene bromide (*v. sup.*) and alcoholic KOH (Reboul a. Truchot, *A.* 144, 248). Alcoholic KOH forms $C_{10}H_{18}$ (165°) and $C_{10}H_{19}OEt$.

Bromo-decylene *v.* MENTHYL BROMIDE.

Di-bromo-decylene $C_{10}H_{18}Br_2$. *Decinene bromide.* Oil. From $C_{10}H_{18}$ and Br (R. a. T.).

Di-bromo-decylene $C_{10}H_{18}Br_2$. From terpilene hydride and Br (Montgolfier, *A. Ch.* [5] 19, 158).

Di-bromo-decylene $C_{10}H_{18}Br_2$. From rutylene and Br (Bauer, *A.* 135, 344).

DI-BROMO-DODECANE $C_{12}H_{24}Br_2$ [−15°]. *Dodecylene bromide.* Formed by the addition of Br_2 to dodecylene (Krafft, *B.* 17, 1371).

BROMO-ISO-DURENE C_6HBrMe_4 [1:3:4:5:6]. (253°). Liquid; solidified by cold (Bielefeldt, *A.* 198, 388).

Bromo-*s*-durene C_6HMe_4Br [1:2:4:5:3]. [61°]. By bromination of durene (Gissmann, *A.* 216, 210). Pearly plates (from alcohol).

Di-bromo-o-durene $C_{10}H_{12}Br_2$ *i.e.* $C_6Me_4Br_2$ [1:2:3:4:5:6]. *Di-bromo-prehnitene.* [210°]. From o-durene, Br, and I. Prisms (Jacobsen, *B.* 19, 1218).

Di-bromo-iso-durene $C_{10}H_{12}Br_2$ [1:3:4:5:2:6]. [209°]. Long fine needles. Sl. sol. hot, v. sl. sol. cold alcohol. Prepared by bromination of iso-durene (Jacobsen, *B.* 15, 1853; *cf.* Jannasch, *B.* 8, 356).

Di-bromo-s-durene $C_6Me_4Br_2$ [1:2:4:5:3:6]. [203°]. Needles (from alcohol) (Fittig a. Jannasch, *Z.* 1870, 161; Friedel a. Crafts, *A. Ch.* [6] 1, 515).

BROMO-DURENOL $C_{10}H_{12}Br.OH$ [118°]. Formed by bromination of durenol in acetic acid. Long prisms. V. sol. alcohol and ether, insol. water (Jacobsen a. Schnapauff, *B.* 18, 2844).

DI-BROMO-ENNANE $C_9H_{18}Br_2$. *Nonylene bromide.* From Br and ennylene (from paraffin). Alcoholic KOH forms bromo-ennylene $C_9H_{17}Br$ (c. 210°) (Thorpe a. Young, *A.* 165, 18).

BROMO-ENNOIC ACID $C_8H_{16}Br.CO_2H$. From ennenoic acid $C_9H_{16}O_2$ and HBr. Decomposed by warm aqueous Na_2CO_3 forming an oil, probably $C_8H_{14}.C_2H_4$ (Schneegans, *A.* 227, 83).

BROMO-ENNYLENE *v.* DI-BROMO-ENNANE.

BROMO-ERUCIC ACID $C_{22}H_{41}BrO_2$. [34°]. From di-bromo-behenic acid and alcoholic KOH. Converted into behenolic acid by alcoholic KOH (Haussknecht, *A.* 143, 50).

Di-bromo-erucic acid $C_{22}H_{40}Br_2O_2$. [47°]. From behenolic acid and bromine (H.).

BROMO-ETHANE *v.* ETHYL BROMIDE.

Di-bromo-ethane *v.* ETHYLENE BROMIDE and ETHYLIDENE BROMIDE.

u-Tri-bromo-ethane $CHBr_2.CH_2Br$. *Bromo-ethylene bromide.* (188°) at 752 mm. S.G. $\frac{17.5}{4}$ 2·6189; $\frac{21.5}{4}$ 2·6107 (Anschütz, *A.* 221, 138). M. M. 12·897 at 11·7°. From $CHBr:CH_2$, water, and Br (Wurtz, *A. Ch.* [3] 51, 84). Also formed by the action of Br on ethyl bromide, ethylene bromide, or iodo-ethylene (M. Simpson, *P. M.* [4] 14, 544; Caventou, *A.* 120, 323; Tawildaroff, *A.* 176, 22; Staedel, *B.* 11, 1741).

Reactions.—1. Alcoholic KOH gives *u*-di-bromo-ethylene, bromo-acetylene, and acetylene. 2. *u*-Di-bromo-ethylene is also formed by the action of alcoholic KOAc, water and PbO, and NaOEt (Michael, *Am.* 5, 192).—3. $SbCl_5$ gives $CHCl_2.CH_2Br$ (Henry, *Bl.* [2] 42, 262).—4. Benzene in presence of Al_2Cl_6 produces bromo-benzene, *s*-di-phenyl-ethane, and *u*-di-phenyl-ethane (Anschütz, *A.* 235, 333).

u-**Tetra-bromo-ethane** $CBr_3.CH_2Br$. *Acetylidene tetrabromide.* (103·5°) at 13·5 mm. S.G. $\frac{21.5}{4}$ 2·9216. From $CBr_2:CH_2$ and Br_2 (Anschütz, *A.* 221, 140; Lennox, *C. J.* 13, 206; Reboul, *A.* 124, 270). Also from tri-bromo-ethane and Br (Denzel, *B.* 12, 2207). Decomposed by heat, giving off Br_2 and HBr. Converted by benzene and Al_2Cl_6 into *u*-di-phenyl-ethane, and *s*-tetra-phenyl-ethane $CHPh_2.CHPh_2$ [210°]: bromo-benzene and acetylene dibromide being also formed (Anschütz, *A.* 235, 196).

s-Tetra-bromo-ethane $CHBr_2.CHBr_2$. *Acetylene tetra-bromide.* (114°) at 12 mm. S.G. $\frac{21.5}{4}$ 2·9629. Acetylene, from $C_2H_4Br_2$ and alcoholic KOH is passed directly into bromine. The product, containing $CHBr_2.CH_2Br$, is treated with alcohol and zinc-dust and CHBr:CHBr is separated from $CH_2:CHBr$ by fractional distillation, and is then mixed with bromine (Anschütz, *A.* 221, 138; *cf.* Reboul, *C. R.* 54, 1229; Sabanejeff, *B.* 9, 1441; *A.* 178, 112).

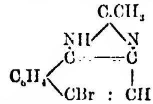
Properties.—Smells of camphor and chloroform. Takes up moisture from air, becoming cloudy. At 185° it begins to decompose, giving off Br_2 and HBr, and leaving C_2HBr_3. With water and bromine at 185° it gives C_2Br_4 and C_2Br_6. Boiling alcoholic KOH forms acetylene and bromo-acetylene. Zinc added to its alcoholic solution forms acetylene dibromide in the cold, but on warming it forms acetylene. With benzene and Al_2Cl_6 it forms bromo-benzene, *u*-di-phenyl-ethane, anthracene, and anthraquinone (Anschütz, *A.* 235, 161). Al_2Cl_6 alone forms $CHBr_2.CH_2Br$ and C_2Br_6. Toluene and Al_2Cl_6 give di-methyl-anthracene [225°]. *o-* *m-* and *p-* xylene appear to give tetra-methyl-anthracenes.

Penta-bromo-ethane $CBr_3.CBr_2H$. [49°] (S.); [54°] (D.); [57°] (B.). (210°) at 300 mm.

Formation.—1. From $CHBr:CBr_2$ and Br (Lennox; Sabanejeff, *A.* 216, 281).—2. From bromo-ethylene and Br (Denzel, *B.* 12, 2208).—3. From bromo-acetylene and Br (Reboul, *A.* 124, 268).—4. By spontaneous decomposition of tri-bromo-ethylene exposed to air (Demole, *Bl.* [2] 34, 204).—5. From acetylene tetrabromide and Br (Bourgoin, *Bl.* [2] 23, 173).—6. From succinic acid, water, and Br (Orlovsky, *J. R.* 9, 280).

Hexa-bromo-ethane C_2Br_6. *Carbon hexa-bromide.* Formed by brominating C_2Br_4H (Reboul). Formed also by the action of Br and Al on CCl_4, C_2Cl_4, or C_2Cl_6 (Gustavson, *J. R.* 13, 287). Also from mucobromic acid, water, and Br at 130° (Delbrück, *A.* 165, 253). Prisms (from CS_2); insol. alcohol. At 200°–210° it decomposes, without previous fusion, into Br and C_2Br_4. Unlike the latter, it is not volatile with steam.

BROMO-ETHENYL-NAPHTHYLENE-DIAMINE



[229°]. Formed by reduction of the acetyl derivative of (1:3:4)-bromo-nitro-(α)-naphthylamine with $SnCl_2$. Small white needles. V. sol. alcohol and ether, insol. water. The ethenyl group is very stable. Salts.—B'HCl.—$B'_2H_2SO_4$: sparingly soluble needles.—$B'HNO_3$: fine white sparingly soluble needles (Prager, *B.* 18, 2160; *cf.* Meldola, *C. J.* 47, 505).

BROMO-ETHOXY- *v.* BROMO-OXY-.

BROMO-ETHYL-ACETO-ACETIC ETHER *v.* BROMO-ACETO-ACETIC ETHER.

d-**Bromo-ethyl-aceto-acetic-ether** $C_8H_{13}BrO_3$ *i.e.* $CH_3.CO.CH(CO_2Et).CH_2.CH_2Br$. Heavy yellowish oil of camphor-like odour. Not distillable. Formed by dissolving trimethylene-methyl-ketone-carboxylic ether $\begin{matrix}CH_2\\ \vert\\ CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CO.CH_3\\ \\ CO_2Et\end{matrix}$ in three times its weight of strongly cooled conc. HBr (1·85 S.G.), allowing to stand 10 mins. at 15° and pouring into iced water. By boiling

with HCl it is converted into acetyl propyl alcohol $CH_3.CO.CH_2.CH_2.CH_2.OH$ (v. p. 46) with formation of alcohol, CO_2, and HBr (Perkin, jun., a. Freer, *C. J.* 51, 833, *B.* 19, 2565).

BROMO-ETHYL ALCOHOL *v.* GLYCOL BROMHYDRIN.

Dibromo-ethyl alcohol $CHBr_2.CH_2OH$. (180°). S.G. $\frac{0}{}$ 2·35. From bromo-ethylene and dilute HBrO (Demole, *B.* 9, 49). Reduces ammoniacal $AgNO_3$. Alcoholic KOH gives bromo-ethylene oxide. *Acetyl derivative* $CHBr_2.CH_2.OAc$. (194°). S.G. $\frac{0}{}$ 1·98.

BROMO-TRI-ETHYL-AMINE. *Ethylo-bromide* $C_2H_4Br.NEt_3Br$. From NEt_3 and ethylene bromide. Alcoholic KOH forms $C_2H_3.NEt_3Br$ (Hofmann, *C. R.* 49, 880).

p-**BROMO-ETHYL-ANILINE** $C_6H_4Br.NHEt$. From *p*-bromo-aniline and EtBr (Hofmann, *A.* 74, 145).

p-**Bromo-di-ethyl-aniline** $C_6H_4Br.NEt_2$. [33°]. (270°). Needles or prisms. Formed by bromination of diethylaniline (Claus a. Howitz, *B.* 17, 1327).

p-**BROMO-ETHYL-BENZENE** C_6H_4BrEt [1:4]. (204°). S.G. $\frac{15.5}{}$ 1·34. From *p*-ethyl-benzene, Br, and I (Kekulé a. Thorpe, *C. J.* 22, 366). From $C_6H_4Br_2$, EtI, and Na (Aschenbrandt, *A.* 216, 222). Does not solidify at −20°. A mixture of *o*- and *p*- ethyl-benzenes is formed by the action of bromine in the dark upon ethyl-benzene, or by the action of bromine in presence of 3 p. c. of iodine upon ethyl-benzene in diffused daylight (Schramm, *B.* 18, 1272).

ω-**Bromo-ethyl-benzene** $C_6H_5.CH_2.CH_2Br$ (c. 148°) at 30 mm. S.G. $\frac{22}{}$ 1·311. Formed by direct combination of styrene with HBr (Bernthsen a. Bender, *B.* 15, 1983). Formed also by treating a mixture of benzene and bromo-ethylene with Al_2Cl_6 (Hanriot a. Guilbert, *C. R.* 98, 525).

a-**Bromo-ethyl-benzene** $C_6H_5.CHBr.CH_3$. (37°) at 17 mm. (c. 150°) at 500 mm. From Br and ethyl-benzene at 140° (Radziszewski, *B.* 6, 492; Berthelot, *C. R.* 67, 328; Anschütz, *A.* 235, 328). Formed also by passing HBr into cooled phenyl-methyl-carbinol (Engler a. Bethge, *B.* 7, 1125). Partially decomposed by distillation into styrene and HBr.

ω-*a*-**Di-bromo-ethyl-benzene** Ph.CHBr.CH_2Br. [74°]. (140°) at 15 mm. *Styrene di-bromide.*

Preparation.—1. From styrene (10 g.), ether (25 g.) and bromine (17 g.) (Blyth a. Hofmann, *A.* 53, 306; Zincke, *A.* 216, 288).—2. From hot ethyl-benzene and Br (Radziszewski, *B.* 6, 493; Friedel a. Balsohn, *Bl.* [2] 35, 55).

Properties.—White plates or needles (from 80 p.c. alcohol). V. e. sol. ether, benzene and glacial HOAc, v. sol. alcohol or benzoline.

Reactions.—1. KOAc and alcohol at 160° gives chiefly *β*-bromo-styrene (150°-160° at 75 mm.).—2. KOAc and glacial HOAc gives chiefly the diacetate of phenyl-glycol, Ph.CH(OAc)CH_2(OAc).—3. Alcoholic KOH or water at 190° give *a*-bromo-styrene (Glaser, *A.* 154, 154).—4. Gives PhCH(OH).CH_2(OH) by treatment with AgOAc, alcohol and AgOBz, or aqueous K_2CO_3. AgOBz in presence of toluene forms Ph.CH(OBz).CH_2(OBz).—5. Benzene and Al_2Cl_6 give *s*-di-phenyl-ethane (Anschütz, *A.* 235, 328).

Tri-bromo-ethyl-benzene $C_6H_5.CHBr.CHBr_2$ [38°]. From *ω*-bromo-styrene and Br (Fittig a. Binder, *A.* 195, 142). Acted upon by benzene and Al_2Cl_6 in presence of CS_2, it is converted into *s*-tetra-phenyl-ethane [209°] (*A.*).

Tetra-bromo-ethyl-benzene $C_8H_6Br_4$. From di-bromo-ethyl-benzene and Br (Kinnicutt a. Palmer, *Am.* 5, 387).

Penta-bromo-ethyl-benzene $C_8H_5Br_5$. From ethyl-benzene, Br, and Al_2Br_6 (Gustavsen, *Bl.* [2] 30, 22).

Di-bromo-di-ethyl-benzene $C_6H_4(C_2H_4Br)_2$. (200°-230°) at 30 mm. From bromo-ethylene, benzene, and Al_2Cl_6 (Hanriot a. Guilbert, *C. R.* 98, 525).

Bromo-tetra-ethyl-benzene $C_6H(C_2H_5)_4Br$ (284° uncor.). Heavy liquid (Galle, *B.* 16, 1745).

Di-bromo-tetra-ethyl-benzene $C_6(C_2H_5)_4Br_2$. [75°]. (above 330°). Prisms. V. sol. alcohol (Galle, *B.* 16, 1745).

BROMO-ETHYL-BROMIDE *v.* DI-BROMO-ETHANE.

BROMO - ETHYL BROMO - ACETATE *v.* BROMO-ACETIC ACID.

BROMO-ETHYLENE C_2H_3Br *i.e.* $CHBr:CH_2$. *Vinyl bromide.* (16°). S.G. $\frac{14}{}$ 1·5167 (Anschütz). Formed by the action of alcoholic KOH upon either di-bromo-ethane (Regnault, *A. Ch.* [2] 59, 358; Beilstein, *J.* 1861, 609; Glöckner, *A. Suppl.* 7, 109; Semenoff, *J.* 1864, 480). Formed also from acetylene and HBr (Reboul, *C. R.* 74, 947). Gas or liquid; when kept in a sealed tube and exposed to sunlight it changes to an amorphous polymeride, insol. water, alcohol, and ether; S.G. 2·075. This substance carbonises when heated (Hofmann, *C. J.* 13, 68; Baumann, *A.* 163, 308); it is not affected by boiling alcoholic KOH. Polymerisation is arrested by the presence of MeI or EtI, but not by chlorinated or brominated hydrocarbons; a little I stops polymerisation of the liquid, but not of the gas. An line arrests, but SO_2 promotes, the change (Lwow, *Bl.* [2] 35, 169).

Reactions.—1. Split up into HBr and acetylene by alcoholic KOH, NaOEt, $NaOC_5H_{11}$, or ammoniacal $AgNO_3$ (Sawitsch, *Bl.* 1861, 7; *A.* 119, 185; Miasnikoff, *Bl.* 1861, 12; *A.* 118, 330).—2. Conc. HBr at 0° forms *s*-di-bromo-ethane; a more dilute acid gives *u*-di-bromo-ethane (Reboul, *A.* 155, 29, 212).—3. Fuming HCl at 100° forms $CH_3.CHBrCl$.—4. Conc. HI at 4° gives $CH_3.CHBrI$; at 100° it forms also $CH_2I.CH_2Br$. (R.).—5. Aqueous solutions of metallic salts either have no action or split it up into acetylene and HBr (Kutscheroff, *B.* 14, 1532; Linnemann, *A.* 163, 347; Saytzeff a. Glinsky, *Z.* [2] 3, 675).—6. Successive treatment with conc. H_2SO_4 and water forms crotonic aldehyde (Zincke, *A.* 191, 370).—7. Aqueous BrOH at 0° gives $CHBr_2.CH_2OH$, $CHBr_2.CH_2Br$, and C_2H_3BrO, [40°-45°] (90°) (Demole, *B.* 9, 49).—7. Dry *oxygen* at 25° has no action.—8. ICl forms $CHBrI.CH_2Cl$ and a less quantity of $CH_2I.CHBrCl$ (Henry, *C. R.* 98, 680).—9. With benzene and Al_2Cl_6 it produces styrene, ethyl-benzene, *u*-di-phenyl ethane, and di-methyl-anthracene dihydride (Anschütz, *A.* 235, 331). If elevation of temperature be avoided and the Al_2Cl_6 be slowly added the products are $C_6H_5.C_2H_4Br$ and $C_6H_4(C_2H_4Br)_2$ (Hanriot a. Guilbert, *C. R.* 98, 525).

s-Di-bromo-ethylene $CHBr:CHBr$. *Acetylene dibromide.* (110°-111°). S.G. $\frac{17.5}{4}$ 2·2714 (Anschütz, *A.* 221, 141); [0] 2·268 (Sabanéeff, *B.* 9, 1441; Plimpton, *C. J.* 39, 536); [12] 2·223 (S.). V.D. 6·47 (calc. 6·44).—Formed by mixing acetylene tetrabromide (100 g.) with alcohol (20 g.) and adding zinc dust slowly, with cooling (A.; *cf.* Sabanéeff, *A.* 216, 252).

Properties.—Oil; does not polymerise.

Reactions.—1. Heated for several days with 50 pts. of *water* at 135°, it is not affected.—2. Heated with dilute K_2CO_3, bromo-acetylene is formed, which is spontaneously inflammable. Alcoholic KOH and aqueous KCy also form bromo-acetylene.—3. Heated with dry KOAc at 160° for two days it forms CHBr:CH(OAc), the acetate of bromo-vinyl alcohol (Sabanéeff, *Bl.* [2] 41, 253).—4. Heated with AgOAc and a little HOAc at 100° it forms a compound $C_2H_2Br_22AgOAc$. This is decomposed by HCl with evolution of acetylene.—5. Combines with $AgNO_3$.—6. With alcoholic KCN it forms a compound which, on saponification, gives an acid $C_4H_6O_4$ [163°-168°]. Its silver salt is $C_4H_4Ag_2O_4$ (S.).—7. Alcoholic KOPh gives CHBr.CHOPh. (c. 223°); S.G. [15] 1·485.—8. With alcoholic NMe_3 at 120° it forms NMe_4Br, NMe_3HBr, NMe_2H_2Br, and carbonaceous bodies:

$$2NMe_3 + C_2H_2Br_2 = 2NMe_3HBr + C_2$$

(Plimpton, *C. J.* 39, 536).—9. With NEt_3 it acts similarly.—10. Acts upon benzene in presence of Al_2Cl_6 forming $CHBr_2.CH_2Br$, anthracene, and $CH_2Ph.CH_2Ph$ (Anschütz, *A.* 235, 153).

u-**Di-bromo-ethylene** $CBr_2:CH_2$. *Acetylidene dibromide.* (92°) at 751 mm. in CO_2. S.G. $\frac{20.6}{4}$ 2·1780 (Anschütz). From $CHBr_2.CH_2Br$ by treatment with alcoholic KOH, NaOEt, sodium, or solid KOH (Cahours, *C. R.* 31, 293; Fontaine, *C. R.* 70, 1361; Sawitsch, *A.* 119, 183; Reboul, *A.* 124, 270; Tawildaroff, *A.* 176, 22; Michael, *Am.* 5, 192). From $CBr_2.CH_2Br$ by boiling with alcohol and KOAc (Demole, *Bl.* [2] 29, 205). or by treatment with zinc and alcohol (Sabanéeff, *A.* 216, 255). Also from $CH_2Cl.CHBr_2$ and alcoholic KOH (Henry, *Bl.* [2] 42, 262).

Properties.—Pungent liquid, attacking the eyes. Readily absorbs oxygen, changing to bromo-acetyl bromide. Polymerises with great ease, becoming solid.

Reactions.—1. HBrO forms $CBr_3.CO.CH_2.CBr_3$ [90°]. S.G. [2] 2·88 (Demole, *B.* 11, 1710).—2. Benzene and Al_2Cl_6 give *u*-di-phenyl-ethylene (Anschütz, *A.* 235, 158).

Tri-bromo-ethylene $CHBr:CBr_2$. (163°-164°). S.G. $\frac{20.5}{}$ 2·708 (S. a. D.); [0] 2·69 (Demole, *B.* 11, 318). From di-bromo-ethylene bromide and alcoholic KOH (Lennox, *A.* 122, 125).

Preparation. — Acetylene tetra-bromide (1 mol.) is dissolved in twice its weight of alcohol and (somewhat more than 2 mols. of) KOAc and Na_2CO_3 (1 mol.) are added; the mixture is heated on a water bath 24 hours with inverted condenser (Sabanéeff a. Dworkowitsch, *A.* 216, 280; *cf.* Sabanéeff, *A.* 178, 122; *Bl.* [2] 29, 207).

Reactions.—1. Alcoholic KOH or Zn and HOEt give a mixture of C_2H_2 and C_2HBr.—2. Alcoholic KOPh at 100° forms phenyl di-bromo-vinyl oxide.—3. Alcoholic KOPh at 170° forms the phenyl derivative of glyoxylic acid, $PhO.CH_2.CO_2H$.—4. Reacts upon benzene in presence of Al_2Cl_6 producing *u*-di-phenyl-ethylene and tri-phenyl-methane (Anschütz, *A.* 235, 336).—5. Absorbs oxygen, becoming $CHBr_2.CO.Br$ (Demole a. Dün, *B.* 11, 1302).

Tri-bromo-ethylene $(C_2HBr_3)_x$. [174°]. A by-product in formation of $C_2H_2Br_4$ from acetylene (Sabanéeff, *A.* 178, 114).

Tetra-bromo-ethylene C_2Br_4. [54°]. (215°).

Formation.—1. By the action of Br on alcohol or ether (Löwig, *A.* 3, 292).—2. From C_2HBr_5 and alcoholic KOH (Lennox, *A.* 122, 126).—3. From CH_2Cl_2 and IBr_3 (Höland, *A.* 210, 234).—4. From CBr_4 by heating at 220° (H.).—5. From di-bromo-succinic acid, Br, and water at 190° (Bourgoin, *B.* 7, 1644).

Properties.—Plates; volatile with steam; not affected by oxygen even at 216° (D.).

BROMO-ETHYL-ETHER *v.* BROMO-ETHYL OXIDE.

BROMO-ETHYL-KAIRINE *v.* Ethyl ether of BROMO-(*B.* 4)-OXY-(*B.* 4)-ETHYL-QUINOLINE TETRAHYDRIDE.

γ-BROMO-ETHYL-MALONIC ACID

$C_5H_7BrO_4$ *i.e.* $Br.CH_2.CH_2.CH(CO_2H)_2$. [116°]. From vinaconic (tri-methylene di-carboxylic) acid and HBr (Röder, *A.* 227, 19; Perkin, jun., *C. J.* 47, 814). Sl. sol. benzene, CS_2 or light petroleum, sol. chloroform. Boiled with water it gives the lactone of γ-oxy-ethyl-malonic acid (*q. v.*).

Bromo-ethyl-malonic acid

$CH_3.CHBr.CH(CO_2H)_2$ (?). [141°]. From crotaconic acid $C_5H_6O_4$ and HBr (Claus, *A.* 191, 79).

TRIBROMO - (α) - ETHYL - NAPHTHALENE $C_{10}H_4Br_3.C_2H_5$. [127°]. Slender needles. Prepared by the action of bromine on (α)-ethyl-naphthalene (Carnelutti, *B.* 13, 1672).

BROMO-ETHYL (β)-NAPHTHYL ETHER *v.* (β)-NAPHTHOL.

ωω-BROMO-DI-ETHYL OXIDE

$CH_2Br.CH_2.OEt$. (128°). S.G. [0] 1·371. V.D. 5·29 (calc. 5·28). From the iodo- compound and Br (Henry, *C. R.* 100, 1007).

Di-ω-bromo-di-ethyl oxide $CH_2Br.CHBr.OEt$. From Br and vinyl ethyl oxide. Very unstable liquid. NaOEt gives $CH_2Br.CH(OEt)_2$ (Wislicenus, *A.* 192, 111).

Tetra-bromo-di-ethyl oxide $C_4H_6Br_4O$. A fuming liquid obtained by saturating ethylidene oxychloride with Br at 120° (Kessel, *B.* 10, 1667).

Octo-bromo-di-ethyl oxide $C_4H_2Br_8O$. (c.134°) at 160 mm. By heating ethylidene oxychloride with Br for 10 hours from 100°-210° (Kessel, *B.* 10, 1667). Fuming oil.

Eso-exo- **DI - BROMO o - ETHYL - PHENOL** $C_6H_3Br(C_2H_4Br)OH$. From *o*-ethyl-phenol and Br in the cold. Decomposed by distillation into HBr and $C_6H_3Br(C_2H_3)OH$ (Suida a. Plohn, *M.* 1, 175).

Tri-bromo-(α)-ethyl-phenol $C_6HBr_3Et.OH$. [55°]. Formed, together with the following body, by treating (α)-ethyl phenol with excess of Br in the cold (Fittig a. Kiesow, *A.* 156, 251).

Eso-exo- **Tri-bromo-ethyl phenol**

$C_6H_3Br(OH).CHBr.CH_2Br$. [108°]. Long white needles. Obtained by the action of alcoholic KOH upon $C_6H_3Br(OH).CHBr.CHBr.CO_2H$, the product of the action of bromine upon *p*-coumaric acid.

Acetyl derivative $C_6H_2Br(OAc).C_2H_3Br_2$: [94°]; needles (Eigel, *B.* 20, 2535).

Tetra-bromo-ethyl phenol $C_6Br_4Et.OH$ [106°] (*v. sup.*).

BROMO-TETRA-ETHYL-PHOSPHONIUM BROMIDE $CH_2Br.CH_2.PEt_3Br$. [235°]. From PEt_3 and ethylene bromide in the cold (Hofmann, *Pr.* 9, 287; *A. Suppl.* 1, 154). Rhombic dodecahedra.

Reactions.—1. Moist silver oxide gives $CH_2(OH).CH_2PEt_3.OH$ (difference from corresponding derivatives of $AsEt_4$ and NEt_4 which give vinyl base).—2. With *silver acetate* and water at 100° it gives acetate of the vinyl base $C_2H_3PEt_3.OAc$.—3. Zinc and H_2SO_4 give tetra-ethyl-phosphonium bromide.—4. Alcoholic *potash* has no effect.—5. Combines with PEt_3, $AsEt_3$ and NH_3 forming di-acid bases.

Salts.—$(C_2H_4Br.PEt_3Cl)_2PtCl_4$. Pale orange monoclinic prisms, sl. sol. cold, v. sol. hot, water.—$(C_2H_4Br.PEt_3Cl)AuCl_3$.—$C_2H_4Br.PEt_3I$.

Hydroxide.—$C_2H_4Br.PEt_3OH$. From the sulphate by the action of baryta. Unstable, rapidly changing to $C_2H_4OH.PEt_3OH$.

BROMO-ETHYL-QUINOLINE $C_9H_6(C_2H_4Br)N$. The hydrobromide is formed by heating quinoline with ethylene bromide.—B'HBr: thick needles.—$(B'_2H_2Cl_2)PtCl_4$: orange-yellow needles (Berend, *B.* 14, 1349).

DI-BROMO-DI-ETHYL SULPHATE $(CH_2Br.CH_2)_2SO_4$. An oil formed by warming Ag_2SO_4 with benzene and ethylene bromide (Beilstein a. Wiegand, *B.* 15, 1369).

Bromo-ethyl-sulphuric acid $CH_2Br.CH_2.O.SO_3H$. From ethylene bromide and SO_3 (Wroblewsky, *Z.* 1868, 563). BaA'_2.—PbA'_2 3aq, scales. An isomeric acid appears to be formed by heating ethylene bromide with Ag_2SO_4 and water (B. a. W.).

BROMO-ETHYL-THIOPHENE $C_4SH_2(C_2H_5)Br$. (195° uncor.). Oil. Formed by shaking ethyl-thiophene with bromine-water (Demuth, *B.* 19, 684).

Di-bromo-(β)-ethyl-thiophene $C_4SHBr_2(C_2H_5)$. Oil. Formed by adding 2 mols. of bromine to 1 mol. of (β)-ethyl-thiophene dissolved in acetic acid (Bonz, *B.* 18, 550).

Tri-bromo-(β)-ethyl-thiophene $C_4SBr_3(C_2H_5)$. [108°]. White plates. Sl. sol. cold alcohol and ether. Formed by complete bromination of (β)-ethyl-thiophene (Bonz, *B.* 18, 549).

BROMO-o-ETHYL-TOLUENE $C_6H_3MeEtBr$ [1:2:4]. (221°). Formed by bromination of o-ethyl-toluene in presence of Fe_2Br_6. Liquid. By HNO_3 (1:1) at 200° it is oxidised to p-bromo-o-toluic acid [118°] (Claus a. Pieszcek, *B.* 19, 3088).

Bromo-p-ethyl-toluene $C_6H_3MeBrEt$ [1:2:4]. From p-ethyl-toluene and Br. Oxidised to bromo p-toluic acid (Morse a. Remsen, *B.* 11, 224).

ωω-Di-bromo-m-ethyl-toluene $C_7H_7.CHBr.CH_2Br$. [45°]. Formed by the combination of m-tolyl-ethylene (m-methyl-styrene) with bromine. Colourless crystals (Müller, *B.* 20, 1216).

Tri-bromo-di-ethyl-toluene $C_6Br_3MeEt_2$. [206°]. From (1, 3, 5)-di-ethyl-toluene (Jacobsen, *B.* 7, 1435).

TRI-BROMO-ETHYL-XYLENE $C_6Br_3EtMe_2$ [3:5:6:1:2:4]. *Tri-bromo-di-methyl-ethyl-benzene.* [91°]. From ethyl-m-xylene (187°) (Anschütz, *A.* 235, 324).

BROMO-EUGENOL $C_6H_2Br(OMe)(OH)C_3H_5$.

Methyl ether $C_6H_2Br(OMe)_2$. (190°) at 20 mm. S.G. $\frac{0}{0}$ 1·396. From the dibromide, hot alcohol, and Zn (Wassermann, *C. R.* 88, 1206). *Di-bromide* $C_6H_2Br_3(OMe)_2$. *Dimethyl ether of di-bromo-di-oxy-propyl-benzene.* [78°]. From Br and a well-cooled solution of methyl-eugenol in ether. Silky needles.

Ethyl ether $C_6H_2Br(OMe)(OEt)$. [48°]. Prepared by the action of alcohol and Zn on its dibromide (Wassermann, *A.* 179, 385). *Di-bromide* $C_6H_2Br_3(OMe)(OEt)$. [80°]. From ethyl-eugenol and Br.

Di-bromo-eugenol $C_6HBr_2(OMe)(OH)(C_3H_5)$. [59°]. Glistening hexagonal prisms. V. sol. alcohol. Formed by boiling an alcoholic solution of the di-bromide with zinc-dust (Chasanowitz a. Hell, *B.* 18, 824).

Di-bromide $C_6HBr_2(OMe)(OH)(C_3H_5Br_2)$. [119°]. Glistening quadratic or trimetric tables. Sparingly soluble in ether and cold alcohol. Formed by bromination of eugenol.

BROMO-FLUORENE

$C_{13}H_9Br$ i.e. $<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_3Br}>CH_2$. [102°]. From fluorene, $CHCl_3$ and Br in the cold (Hodgkinson a. Matthews, *C. J.* 43, 165). Needles (from alcohol). V. sol. $CHCl_3$. Oxidises to bromo-di-phenylene ketone.

(α)-Di-bromo-fluorene

$C_{13}H_8Br_2$ i.e. $<\genfrac{}{}{0pt}{}{C_6H_3Br}{C_6H_3Br}>CH_2$. *Di-bromo-di-phenylene-methane.* [165°] (Barbier, *A. Ch.* [5] 7, 479; Hodgkinson a. Matthews, *C. J.* 43, 164). Got by adding bromine to a solution of fluorene in $CHCl_3$. Monoclinic crystals, $a:b:c$ = 1·167:1:1·065; β = 77° 52′ (Arzruni, *Z. Kryst.* 1, 624). Sol. boiling alcohol. Turned yellowish by light. CrO_3 gives di-bromo-di-phenylene ketone.

Sulphonic acid $C_{13}H_7Br_2SO_3H$. [142°]. Formed by sulphonation with $ClSO_3H$ in $CHCl_3$.—BaA'_2.

(β)-Di-bromo-fluorene $C_{13}H_8Br_2$. [163°]. Formed together with the preceding (Fittig a. Schmitz, *A.* 193, 134). Monoclinic crystals; $a:b:c$ = ·563:1:·697. β = 78° 21′ (A.). Readily changes into two isomeric modifications (γ) and (δ) (Lehmann, *Z. Kryst.* 1, 626).

Tri-bromo-fluorene

$C_{13}H_7Br_3$ i.e. $<\genfrac{}{}{0pt}{}{C_6H_3Br}{C_6H_3Br}>CHBr$. [162°]. From fluorene (1 mol.) in CS_2 and Br (3 mols.). Oxidised by CrO_3 to (β)-di-bromo-diphenylene ketone (B.).

DI-BROMO-FLUORESCEÏN $C_{20}H_{10}Br_2O_5$. [260°-270°]. From fluorescein (1 mol.) and Br (2 mols.) in HOAc (Baeyer, *A.* 183, 1). Reddish-brown needles with green reflex. Dyes wool and silk salmon-pink.

Di-acetyl derivative $C_{20}H_8Ac_2Br_2O_5$. [210°].

Tetra-bromo-fluoresceïn

$C_{20}H_8Br_4O_5$ i.e. $O<\genfrac{}{}{0pt}{}{C_6HBr_2(OH)}{C_6HBr_2(OH)}>C<\genfrac{}{}{0pt}{}{C_6H_4}{O}>CO$.

Eosin. Formed by adding Br to a solution of fluorescein in HOAc. It is purified by conversion into the K salt (Baeyer, *A.* 183, 38). Prepared by dissolving fluorescein (1 mol.) in

NaOHAq, adding a solution of Br (4 mols.) in NaOHAq, and acidifying. Orange needles (containing HOEt) (from alcohol), or flesh-coloured crystals $C_{20}H_8Br_4O_6$ (from dilute alcohol containing HCl). Tetra-bromo-fluoresceïn is v. sl. sol. water and benzene; its alkaline solutions are pink and show strong yellow fluorescence, they dye wool and silk pink. Zinc-dust and NaOH reduce it to a leuco-compound, which is reoxidised by air. Potash-fusion forms di-bromo-resorcin and di-bromo-resorcin-phthaleïn. Conc. H_2SO_4 forms $C_{40}H_{13}Br_7O_{10}$. PCl_5 forms $C_{20}H_6Cl_2Br_4O_3$. Sodium-amalgam forms fluoresceïn. Warming with conc. KOH gives a deep blue solution whence HCl pps. unstable

$$O<\genfrac{}{}{0pt}{}{C_6HBr_2(OH)}{C_6HBr_2(OH)}>C(OH).C_6H_4.CO_2H.$$

Salts. — $K_2(C_{20}H_6Br_4O_5)$ 5aq. S. 50. — $K_2A''HOEt$. — $(NH_4)_2A''$. — $BaA''2aq$. — $CaA''\frac{1}{2}aq$. — Ag_2A''. — $(HOPb)_2A''$.

Methyl ether $C_{20}H_7MeBr_4O_5$. *Methyl erythrin.*

Ethyl ether $C_{20}H_7EtBr_4O_5$. *Erythrin. Spirit-soluble eosin.* From K_2A'', $KEtSO_4$, and alcohol at 150°. From fluoresceïn, boiling alcohol and Br. Red crystals (from alcohol). Formed, together with a colourless ethyl-eosin, by heating silver eosin with EtI and alcohol at 100°. — $KC_{20}H_6EtBr_4O_5aq$: dyes a more violet shade than eosin.

Di-ethyl ether $C_{20}H_6Et_2Br_4O_5$. From Ag_2A'' and EtI.

Acetyl derivative $C_{20}H_6Ac_2Br_4O_5$ (?). [278°].

BROMOFORM $CHBr_3$. *Tri-bromo-methane.* Mol. w. 253. [8°]. (151°). S.G. $\frac{0}{4}$ 2·8341 (T.); $\frac{15}{4}$ 2·9045 (Perkin, *C. J.* 45, 533); $\frac{15}{15}$ 2·8842 (P.). C.E. (0°-10°) ·000944; (0°-100°) ·0010116. S.V. 103·53 (Thorpe, *C. J.* 37, 203). M.M. 11·626 at 17·9° (P.). V.D. 8·63 (calc. 8·75) (Cahours, *A. Ch.* [3] 19, 481).

Occurrence.—In crude bromine (Hermann, *A.* 95, 211; Dyson, *C. J.* 43, 36).

Formation.—1. By the simultaneous action of Br and KOH, or of 'bromide of lime,' on alcohol or acetone, or by decomposing bromal with alkalis (Löwig, *A.* 3, 295; Dumas, *A. Ch.* [2] 56, 120; Günther, *Ar. Ph.* [3] 25, 373). — 2. From CH_2Cl_2 and IBr_3 (Höland, *A.* 240, 236).

Reactions. — 1. Alcoholic KOH forms CO (3 vols.) and ethylene (1 vol.) but no formate (Long, *A.* 194, 23). — 2. Br in presence of dilute KOH in sunlight forms CBr_4 (Habermann, *B.* 6, 549). 3. Reduced to CH_4 by KI, water, and Zn or Cu (Berthelot, *A. Ch.* [3] 51, 48) or by the copper zinc couple (Gladstone a. Tribe, *C. J.* 28, 510).

BROMO-FUMARIC ACID $C_2HBr(CO_2H)_2$. [178°].

Formation.—1. From iso-di-bromo-succinic acid by heating at 180° or by boiling with water (Kekulé, *A. Suppl.* 2, 91; *A.* 130, 1). — 2. From di-bromo-succinic acid and water at 140° (Bandrowski, *B.* 12, 345). — 3. By dissolving acetylene-di-carboxylic acid in strong aqueous HBr (Bandrowski, *B.* 15, 2697). — 4. From ($\beta\delta$)-dibromopyromucic acid and from (β)-bromo-pyromucic acid by dilute HNO_3 (Hill a. Sanger, *A.* 232, 82, 61). 5. From bromo-maleïc acid and cold fuming HBr (Fittig a. Petri, *A.* 195, 67)

Properties.—Laminæ; v. e. sol. water, v. sol. alcohol and ether. At 200° it changes to bromo-maleïc acid or its anhydride. Sodium-amalgam forms fumaric acid. Br gives the same tri-bromo-succinic acid as with bromo-maleïc acid. Fuming HBr combines slowly in the cold; at 100° it quickly forms iso-di-bromo-succinic acid. With its equivalent of aniline it unites immediately to form the acid aniline salt. This does not give an anilide on standing for weeks in contact with cold water. On boiling its aqueous solution the same substance is obtained as on heating aniline bromo-maleate, viz. $C_{16}H_{12}N_2O_2$. [230°] (Michael, *Am.* 9, 180).

Salts.—Ag_2A''.—$PbA''2aq$.—$A''H(NH_3Ph)$: [154°] (Michael, *B.* 19, 1373).

Dimethyl ether $A''Me_2$. [30°] (Anschütz, *B.* 12, 2281).

Di-bromo-fumaric acid

$CO_2H.CBr:CBr.CO_2H$. [220°]. Colourless crystals. Prepared by the addition of bromine to acetylene-dicarboxylic acid. On distillation it is converted into dibromomaleïc acid [108°].

Salts.—$Ag_2A''\frac{1}{2}aq$. - PbA'' (Bandrowski, *B.* 12, 2213).

(β)-BROMO-FURFURANE C_4H_3BrO. (103°). From the corresponding bromo-pyromucic acid by distilling with lime (Canzoneri a. Oliveri, *G.* 17, 42). Heavy oil.

(α)-Di-bromo-furfurane $C_4H_2Br_2O$ *i.e.*

$$\begin{matrix} HC\cdot CBr \\ | \\ HC\cdot CBr \end{matrix}\!\!>O.$$ [10°]. (63°) at 15 mm.; (165°) at 764 mm. Formed by adding bromine to an alkaline solution of (δ)-bromo-pyromucic acid [184°]. On oxidation it gives fumaric and maleïc acids.

Tetra-bromide $C_4H_2Br_6O$: [111°]; by long boiling with water it yields bromo-fumaric and bromo-maleïc acids (Hill a. Hartshorn, *B.* 16, 1132; *B.* 18, 448; *A.* 232, 53).

(β)-Di-bromo-furfurane $<\genfrac{}{}{0pt}{}{CBr:CH}{CBr:CH}>O$. (166°). Formed by distilling di-bromo-pyromucic acid (1 pt.) with $Ca(OH)_2$ (2 pts.) (Canzoneri a. Oliveri, *G.* 15, 116).

Tetra-bromo-furfurane C_4Br_4O [65°]. From ($\beta\gamma$)-di-bromo-pyromucic acid, or from tri-bromo-pyromucic acid, water and bromine vapour. Formed also by the action of alcoholic KOH on di-bromo-furfurane tetrabromide (Hill a. Sanger, *A.* 232, 86, 96; *B.* 16, 1132; 17, 1760).

Di-bromide C_4Br_6O. [123°]. Six-sided plates. V. sol. ether, m. sol. alcohol and benzene. By boiling with water it yields di-bromo-maleïc acid (Hill a. Hartshorn, *B.* 18, 450).

BROMO-FURIL v. FURIL.

BROMO-GALLIC ACID v. BROMO-TRI-OXY-BENZOIC ACID.

TRI-BROMO-GUAIACOL $C_7H_5Br_3O_2$ *i.e.* $C_6HBr_3(OMe)(OH)$. [102°]. From guaiacol and Br (Tiemann a. Koppe, *B.* 14, 2017).

BROMO-GUANIDINE CH_4BrN_3. From guanidine carbonate and Br (Kamenski, *B.* 11, 1600). Needles; detonates just above 100°.

BROMO-GUANINE $C_5H_4N_5OBr$. From guanine and bromine, crystallised from water. White powder. Sl. sol. boiling water, insol. cold water, alcohol or ether.—B'HCl. Prisms.

Converted by $NaNO_2$ into bromo-xanthine (Fischer a. Reese, *A.* 221, 341).

TRI-BROMO-HEMIMELLITHOL *v.* TRI-BROMO-TRI-METHYL-BENZENE-(1:2:3:4:5:6).

BROMO-HEPTANE *v.* HEPTYL BROMIDE.

Di-bromo-heptane $C_7H_{14}Br_2$. *Heptylene bromide.* S.G. $\frac{18.5}{}$ 1·515. From heptane of paraffin oil. Decomposes at 150° (Thorpe a. Young, *A.* 165, 12).

Di-bromo-heptane $C_7H_{14}Br_2$ (211°). From heptane in the oil of *Pinus sabiniana* (Venable, *A. C. J.* 4, 22).

Di-bromo-heptane $CMe_3.CMeBr.CH_2Br$. From penta-methyl-ethyl alcohol and PBr_5. Easily fusible solid (Kaschirski, *C. C.* 1881, 278).

Di-bromo-heptane $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CHBr_2$. *Heptylidene bromide.* From œnanthol and PCl_3Br_2 (Bruylants, *B.* 8, 409).

Hexa-bromo-heptane $C_7H_{10}Br_6$. From heptonene and Br. Oil (Saytzeff, *A.* 185, 144).

a-BROMO-HEPTOIC ACID $C_7H_{13}BrO_2$ *i.e.* $CH_3.CH_2.CH_2.CH_2.CH_2.CHBr.CO_2H$ (250°). From Br and heptoic acid (Cahours, *A. Suppl.* 2, 83; Helms, *B.* 8, 1168; Hell a. Schüle, *B.* 18, 625).

Ethyl ether EtA'. (c. 225°). S.G. $\frac{0}{4}$ 1·211.

TETRA-BROMO-HEPTYL ALCOHOL $C_7H_{12}Br_4O$ *i.e.* $(CH_2Br.CHBr.CH_2)_2CH.OH$. From di-allyl-carbinol and Br (M. Saytzeff, *A.* 185, 135). Oil.

Acetyl derivative $C_7H_{11}Br_4OAc$. Converted by AgOAc into $C_7H_{11}O(OAc)_3$, S.G. $\frac{0}{0}$ 1·180, whence baryta forms a syrup $C_7H_{11}O(OH)_3$ (Dieff, *J. pr.* [2] 35, 17).

BROMO-HEPTYLENE $C_7H_{13}Br$. (158°). From the heptylene bromide of Venable.

Bromo-heptylene $C_7H_{13}Br$. (165°). From the heptylene bromide of Bruylants.

BROMO-HEXADECANE *v.* CETYL BROMIDE.

Di-bromo-hexadecane $C_{16}H_{32}Br_2$. *Cetene bromide.* [13½]. Colourless crystalline solid. Formed by addition of Br_2 to cetene (Krafft, *B.* 17, 1373).

BROMO-HEXANE *v.* HEXYL BROMIDE.

Di-bromo-hexane $C_6H_{12}Br_2$ *i.e.* $CH_3.CH_2.CH_2.CHBr.CHBr.CH_3$. (196°) at 740 mm. S.G. $\frac{15}{}$ 1·5809. From the corresponding hexylene (Erlenmeyer a. Wanklyn, *A.* 135, 141; *cf.* Hecht a. Strauss, *A.* 172, 69; Hecht, *B.* 11, 1423).

Di-bromo-hexane $Me_2CBr.CBrMe_2$ [170°] (K.); [140°] (E.). From $Me_2C:CMe_2$ and Br. Needles (from ether). Converted by heating with water and PbO at 150° into pinacolin (Pawlow, *A.* 196, 124; Eltekoff, *J. R.* 10, 220; Kaschirsky, *J. R.* 13, 81).

Di-bromo-hexane $Me_3C.CHBr.CH_2Br$. From $Me_3C.CH:CH_2$. Crystalline (Friedel a. Silva, *Bl.* [2] 19, 289).

Di-bromo-hexane $C_6H_{12}Br_2$. (211°). From hexane of petroleum (Pelouze a. Cahours, *A.* 124, 293).

Tetra-bromo-hexane $C_6H_{10}Br_4$. *Diallyl-tetrabromide.* [63°]. From diallyl and Br (Wagner a. Tollens, *B.* 6, 588).

Tetra-bromo-hexane $C_6H_{10}Br_4$. [112°]. From iodo-hexylene and Br (Bouchardat, *Z.* 1871, 699).

Tetra-bromo-hexane $C_6H_{10}Br_4$. From hexinene derived from mannite (Hecht, *B.* 11, 1054).

Tetra-bromo-hexane $C_6H_{10}Br_4$. From hexinene from di-methyl-allyl-carbinyl chloride (Saytzeff, *B.* 11, 2152).

Tetra-bromo-hexane $C_6H_{10}Br_4$. [112°]. (318° cor.). From hexinene derived from coal-tar (Schorlemmer, *A.* 139, 250).

Hexa-bromo-hexane $C_6H_8Br_6$. From diallylene (Henry, *Bn.* 1, 199).

Hexa-bromo-hexane $C_6H_8Br_6$. [77°]. From di-bromo-diallyl (Henry, *B.* 7, 23).

Hexa-bromo-hexane $C_6H_8Br_6$. [152°]. From *sec* hexyl iodide and Br at 130° (Merz a. Weith, *B.* 11, 2250).

Hexa-bromo hexane $C_6H_8Br_6$. From hexane and Br at 125° (Wahl, *B.* 10, 1234).

Octo-bromo-hexane $C_6H_6Br_8$. From hexane and Br (W.).

Octo-bromo-hexane $C_6H_6Br_8$. [135°]. From *sec*-hexyl iodide and Br at 130° (M. a. W.).

Octo-bromo-hexane $C_6H_6Br_8$. *Dipropargyl octobromide* [141°] (Henry, *B.* 7, 21).

BROMO-HEXENOIC ACID $C_6H_8Br_2O_2$. *Di-bromo-hydrosorbic acid.* [95°]. From sorbic acid and Br. Laminæ (Fittig a. Kachel, *A.* 168, 287).

DI-BROMO-HEXINENE $C_6H_8Br_2$. *Di-bromo-diallyl.* (210°). S.G. $\frac{18}{}$ 1·656. From diallyl-tetra-bromide and solid KOH (Henry, *J. pr.* [2] 8, 57).

Tetra-bromo-hexinene $C_6H_6Br_4$. *Propargyl tetrabromide.* S.G. $\frac{0}{}$ 2·464. Liquid (Henry, *B.* 6, 959).

a-BROMO-n-HEXOIC ACID $CH_3.CH_2.CH_2.CH_2.CHBr.CO_2H$. *Bromo-caproic acid.* (240°). From caproic acid and Br (Cahours, *A. Suppl.* 2, 78).

Ethyl ether EtA' (205°–210°) (Hell, *B.* 17, 2218).

γ-Bromo-n-hexoic acid $CH_3.CH_2.CHBr.CH_2.CH_2.CO_2H$. From hydrosorbic, or iso-hydrosorbic, acid and HBr. Oil. Sodium-amalgam reduces it to *n*-hexoic acid. Boiling water converts it into hydrosorbic and oxy-hexoic acids (Fittig, *A.* 200, 42; Hjelt, *B.* 15, 618).

γ-Bromo-iso-hexoic acid $Me_2CBr.CH_2.CH_2.CO_2H$.

Ethyl ether A'Et. Formed by saturating an absolute alcoholic solution of isocaprolactone with HBr. By distillation it is decomposed into the original lactone and EtBr (Bredt, *B.* 19, 514).

Bromo-hexoic acid $C_6H_{11}BrO_2$. [86°]. From iso-pyroterebic acid and HBr. Prisms. AgA' (Lagermark a. Eltekoff, *J. R.* 11, 125).

Bromo-hexoic acid $C_6H_{11}BrO_2$. [25°]. From ethyl-crotonic acid and conc. HBrAq. Sodium-amalgam forms hydro-ethyl-crotonic acid. Aqueous Na_2CO_3Aq even at 0° forms amylene, NaBr, and CO_2.

aβ-Di-bromo-iso-hexoic acid $Pr.CHBr.CHBr.CO_2H$ [99°]. From pyroterebic acid and Br (W. S. Williams, *B.* 6, 1095; Geisler, *A.* 208, 46). Large crystals (from CS_2).

Di-bromo-hexoic acid $C_6H_{10}Br_2O_2$. [68°]. From sorbic acid and fuming HBr. Boiling water or alkalis produce sorbic acid, and other bodies (*cf.* Hjelt, *B.* 15, 620).

Di-bromo-hexoic acid $C_6H_{10}Br_2O_2$. From hydrosorbic acid and Br in CS_2. Liquid; decomposed by boiling water, giving oxy-hydrosorbic acid (Fittig, *A.* 161, 314; 200, 46; Hjelt, *B.* 15, 619).

Di-bromo-hexoic acid $C_6H_{10}Br_2O_2$. From iso-sorbic acid and HBr. Oil (L. a. E.).

Di-bromo-hexoic acid CHEtBr.CMeBr.CO_2H. [98°]. From methyl-ethyl-acrylic acid and Br. Monoclinic crystals, $a:b:c = \cdot96:1:1\cdot53$. $\beta =$ 94° 36'. Water at 100° forms bromo-amylene CHEt:CMeBr, methyl-ethyl-acrylic acid, di-oxy-hexoic acid, and methyl ethyl ketone (Lieben, a. Zeisel, *M.* 4, 78).

Di-bromo-hexoic acid $C_6H_{10}Br_2O_2$. [81°]. From ethyl-crotonic acid and Br. Decomposed by cold Na_2CO_3Aq into bromo-amylene, NaBr, and CO_2 (Fittig, *A.* 200, 35).

Tetra-bromo-hexoic acid $C_6H_8Br_4O_2$. [183°]. From sorbic acid and Br (Fittig, *A.* 161, 323; 168, 277; 200, 58). Monoclinic crystals (from alcohol). More stable than the preceding acids, not being attacked by water at 100°. – NaA' 2aq. —CaA'$_2$ 7aq. BaA'$_2$ 1½aq.

DI-BROMO-HEXOIC ALDEHYDE $C_6H_{10}Br_2O$ *i.e.* $CH_3.CH_2$.CHBr.CMeBr.CHO. *Di-bromo-methyl-propyl-acetic aldehyde.* From Br and cold methyl-ethyl-acroleïn. Pungent oil. – ($C_6H_{10}Br_2O$)$NaHSO_3$ 3aq (Lieben a. Zeisel, *M.* 4, 19).

BROMO-HEXONENE C_6H_7Br. *Bromo di-allylene.* (150°). From di-bromo di-allyl and KOH. Pps. ammoniacal $AgNO_3$ and cuprous chloride (Henry, *B.* 14, 400).

Octo-bromo-hexonene C_6Br_8. From *sec*-hexyl iodide and Br at 140°. Prisms. At 200° it splits up into Br and hexa-bromo-benzene (Merz a. Weith, *B.* 11, 2247).

BROMO-HEXYL ALCOHOL $C_6H_{13}BrO$ *i.e.* CH_3.CHBr.CH(OH).CH_2Et. (189°). S.G. 1·3. Liquid. From hexylene oxide and Br (Henry, *C. R.* 97, 260; *Bl.* [2] 41, 363).

Di-bromo-hexyl alcohols *v. Dibromides of* HEXENYL ALCOHOLS.

DI BROMO-HEXYL-BENZENE $C_{12}H_{16}Br_2$ *i.e.* Ph.CHBr.CHBr.CH_2.CH(CH_3)$_2$. [80°]. From hexyl-benzene (*q. v.*). Needles or plates.

BROMO HEXYLENE $C_6H_{11}Br$. (138°-141°) at 739 mm. S.G. ° 1·2025. From (β)-hexylene bromide and alcoholic KOH (Caventou, *A.* 135, 126; Reboul a. Truchot, *A.* 144, 247; Hecht, *B.* 11, 1424; *A.* 172, 70). See also HEXENYL BROMIDE.

Di-bromo-hexylene $C_6H_{10}Br_2$. S.G. ° 1·698. From hexylene (derived from mannite) and Br (Henry, *B.* 11, 1054).

Tetra-bromo-hexylene $C_6H_8Br_4$. From di-allylene and Br (Henry, *C. R.* 87, 171).

Octo-bromo-hexylene $C_6H_4Br_8$. [184°]. From *sec*-hexyl iodide and Br at 130° (Merz a. Weith, *B.* 11, 2249; Hecht, *B.* 11, 1120).

Octo-bromo-hexylene $C_6H_4Br_8$. From hexane and Br at 125° (Wahl, *B.* 10, 402).

BROMO-HIPPURIC ACID $C_9H_8BrNO_3$ *i.e.* C_6H_4Br.CO.NH.CH_2.CO_2H. From hippuric acid, alcohol, and Br. Slender needles. Possibly identical with the following acid.– CaA'$_2$ (Mayer, *Z.* 1865, 415).

p-**Bromo-hippuric acid** [1:4] C_6H_4Br.CO.NH.CH_2.CO_2H. Excreted when *p*-bromo-toluene is taken with food. Flat needles (from water). Boiling HClAq forms glycocoll and *p*-oxy-benzoic acid (Preusse, *H.* 5, 63).

BROMO-HYDRATROPIC ACID *v.* BROMO-PHENYL-PROPIONIC ACID.

BROMHYDRIN *v.* GLYCERIN.

Tri-bromhydrin *v.* TRI-BROMO-PROPANE.

p-**BROMO-HYDROCARBOSTYRIL** C_9H_8BrNO *i.e.* $C_6H_3(Br)\Big<\begin{matrix}C_2H_4.CO\\NH\end{matrix}\Big>$ $\left[4:\frac{1}{2}\right]$. [178°]. Long flat needles. V. sol. alcohol, ether, benzene and acetic acid. Prepared by reduction of *p*-bromo-*o*-nitro-hydro-cinnamic acid with tin and HCl (Gabriel a. Zimmermann, *B.* 13, 1683).

BROMO-HYDROCINNAMIC ACID *v.* BROMO-PHENYL-PROPIONIC ACID.

DI-BROMO-HYDRO-CŒRULIGNON *v.* CŒRULIGNON.

BROMO-HYDROQUINONE $C_6H_5BrO_2$ *i.e.* $C_6H_3Br(OH)_2$. [111°].

Formation.—1. Together with di-bromo-hydroquinone, by the action of conc. HBrAq on quinone (Wichelhaus, *B.* 12, 1504).—2. From hydroquinone (1 mol.) and Br (1 mol.) in ether-chloroform (Sarauw, *A.* 209, 99).

Properties.—Leaflets; may be sublimed. V. e. sol. water, alcohol, and benzene. Fe_2Cl_6 forms bromoquinone.

Di-acetyl derivative $C_6H_3Br(OAc)_2$. [73°]. Formed, together with di-acetyl di-bromo-hydroquinone by heating quinone with AcBr (Schulz, *B.* 15, 655). Needles, sol. alcohol and benzene.

Di-bromo-hydroquinone $C_6H_2Br_2(OH)_2$. [187°].

Formation.—1. As above (W.).—2. From hydroquinone and Br in HOAc (Benedikt, *M.* 1, 345).—3. From quinone and Br (Sarauw).

Properties.—Long needles (from water). Converted by Fe_2Cl_6 or bromine-water into di-bromoquinone.

Di-acetyl derivative $C_6H_2Br_2(OAc)_2$. [161°]. Formed as above (Schulz). Needles, sol. chloroform and ether.

Methyl ether $C_6H_2Br_2$(OH)(OMe). From methyl-hydroquinone and Br (B.).

Di-methyl ether $C_6H_2Br_2(OMe)_2$. [142°]. From di-methyl-hydroquinone and Br in HOAc (Habermann, *B.* 11, 1036). Methyl-ethyl ether $C_6H_2Br_2$(OMe)(OEt). [88°]. Prepared like the preceding (Fiala, *M.* 6, 913).

Di-isobutyl ether $C_6H_2Br_2(OC_4H_9)_2$. From $C_6H_4(OC_4H_9)_2$ and Br (Schubert, *M.* 3, 684). Plates (from HOAc).

Di-bromo-hydroquinone C_6H_3Br(OH)(OBr) (?). *Bromoxy-bromo-phenol.* [87°]. From quinone (1 mol.) and Br (1 mol.) in chloroform (Sarauw). Golden tables, sl. sol. ether and $CHCl_3$, decomposed by water into HBr and bromoquinone; changes slowly to $C_6H_2Br_2(OH)_2$.

Tri-bromo-hydroquinone $C_6HBr_3(OH)_2$. [136°]. Formed together with tetra-bromo-hydroquinone, by treating di-bromo-quinone with conc. HBr, or by the action of Br (6 mols.) on hydroquinone (2 mols.) or quinone (3 mols.) (Sarauw, *A.* 209, 116). Silky needles, sol. alcohol and benzene, v. sol. boiling water. Fe_2Cl_6 gives tri-bromo-quinone.

Tetra-bromo-hydroquinone $C_6Br_4(OH)_2$. [244°]. Prepared as above (Sarauw). Prepared also by reducing tetra-bromo-quinone (bromanil) with SO_2 or HI and P (Stenhouse, *A.* 91, 310; *Suppl.* 8, 20) or by warming it with conc. HBrAq. Slender needles (from HOAc); insol. boiling water, v. sol. alcohol. Fe_2Cl_6 forms tetra-bromo-quinone.

BROMO-HYDROQUINONE-PHTHALEÏN v. HYDROQUINONE-PHTHALEÏN.

DI-BROMO-HYDROSORBIC ACID v. BROMO-HEXENOIC ACID.

BROMO-HYDRO-THYMOQUINONE $C_{10}H_{13}BrO_2$ *i.e.* $C_6H(C_3H_7)(CH_3)Br(OH)_2$. [58°]. From thymoquinone and HBr (Schniter, *B.* 20, 1318). Oxidises to bromothymoquinone [45°]. The di-acetyl derivative is formed by the action of acetyl-bromide on thymoquinone.

Di-acetyl derivative [91°]. Rhombohedral crystals (Schulz, *B.* 15, 657).

Di-bromo-hydro-thymoquinone $C_6(C_3H_7)(CH_3)Br_2(OH)_2$.

Di-acetyl derivative [122°]. Colourless tables (Schulz, *B.* 15, 658).

BROMO-HYDRO-TOLUQUINONE $C_6H_2MeBr(OH)_2$. [c. 160°]. Formed by the action of cold conc. HBr upon toluquinone. Glistening plates (Schniter, *B.* 20, 2286).

Tri-bromo-hydro-toluquinone $C_7H_5Br_3O_2$ *i.e.* $C_6Br_3Me(OH)_2$. [202°]. From tri-bromo-toluquinone and SO_2. Needles, sol. water (Canzoneri a. Spica. *G.* 12, 471).

BROMO - HYPOGÆIC ACID v. HYPOGÆIC ACID.

DI - BROMO - ICOSYLENE $C_{20}H_{38}Br_2$. Oil. From icosinene and Br (Lippmann a. Hawliczek, *B.* 12, 69).

DI-BROMO-INDIGO $C_{16}H_8Br_2N_2O_2$ *i.e.*

$$C_6H_3Br\left<\begin{matrix}\overset{O}{C}\\ \underset{H}{N}\end{matrix}\right>C = C\left<\begin{matrix}\overset{O}{C}\\ \underset{H}{N}\end{matrix}\right>C_6H_3Br.$$

Formed by boiling ω-di-bromo-*m*-bromo-*o*-amido-acetophenone [5:2:1] $C_6H_3Br(NH_2).CO.CHBr_2$ or ω-di-chloro-*m*-bromo-*o*-amido-acetophenone [5:2:1] $C_6H_3Br(NH_2)CO.CHCl_2$ or their acetyl derivatives with dilute NaOH and exposure to the air (Baeyer a. Bloem, *B.* 17, 968). Prepared by heating bromo-isatin with PCl_5 and treating the product with a 10 p.c. solution of HI in acetic acid and then with aqueous SO_2. Some isomeric di-bromo-indipurpurin is formed at the same time (Baeyer, *B.* 12. 1315). Small black needles, may be sublimed; v. sl. sol. most menstrua. May be reduced to a 'vat' like indigo.

BROMO-INDIRUBIN $C_{16}H_9BrN_2O_2$. Long needles. Formed by the action of Na_2CO_3 on an alcoholic solution containing indoxyl and bromo-isatin (Baeyer, *B.* 14, 1745).

ββ-BROMO-IODO-ACRYLIC ACID $C_3H_2IBrO_2$ *i.e.* $CBrI{:}CH.CO_2H$. [110°]. S. 1·7 at 20°. From bromo-propiolic acid and HI (Hill, *Am.* 3, 175). Scales.—BaA'_2 3aq. S. (of BaA'_2) 16 at 20°.—CaA'_2 3½aq.—AgA'.

αβ-Bromo-iodo-acrylic acid $CHI{:}CBr.CO_2H$. [96°]. Formed by the addition of HBr to β-iodo-propiolic acid (Homolka a. Stolz, *B.* 18, 2284). Needles; sl. sol. cold water. By heating in alcoholic solution with AgBr it yields αβ-di-bromo-acrylic acid [85°] (Stolz, *B.* 19, 537).

βα-Bromo-iodo-acrylic acid $CHBr{:}CI.CO_2H$. [71°]. Colourless crystals. V. sol. water. Formed by boiling propiolic acid with an ethereal solution of BrI (Stolz, *B.* 19, 536).

ββα-Bromo-di-iodo-acrylic acid $CBrI{:}CI.CO_2H$. [160°]. S. 2 at 20°. From bromo-propiolic acid and iodine in ether. Flat six-sided plates.—BaA'_2 4aq. S. 15·26 at 20°.—CaA'_2.—KA'.—AgA' (Mabery a. Lloyd, *Am.* 8, 124).

αββ-Bromo-di-iodo-acrylic acid $CI_2{:}CBr.CO_2H$. [182°]. Glistening colourless plates. Formed by the action of iodine bromide upon iodo-propiolic acid in ethereal solution (Homolka a. Stolz, *B.* 18, 2286).

ββα-Di-bromo-iodo-acrylic acid $CBr_2{:}CI.CO_2H$. [110°]. S. 3·5 at 20°. From bromo-propiolic acid and IBr (Mabery a. Lloyd, *Am.* 4, 94; *N. Am. A.* 17, 94). Monoclinic prisms (from water); *a:b:c* = ·617:1:·581.—BaA'_2 3½aq. S. 16·7 at 20°. CaA'_2.—AgA'.

βαβ-Di-bromo-iodo-acrylic acid $CIBr{:}CBr.CO_2H$. [147°]. Long silky needles. Sl. sol. cold water. Formed by the action of a solution of bromine in chloroform upon iodo-propiolic acid $IC{:}C.CO_2H$ (Homolka a. Stolz, *B.* 18, 2285).

DI-BROMO-IODO-ALLYL ALCOHOL.

Ethyl ether $C_5H_7Br_2IO$ *i.e.* $CIBr{:}CBr.CH_2.OEt$. Oil. From iodo-propargyl ethyl ether and Br (Liebermann, *A.* 135, 286).

***o*-BROMO-IODO-BENZENE** C_6H_4BrI [1:2]. (257°). From *o*-bromo-aniline or *o*-iodo-aniline by the diazo- reaction (Körner, *G.* 4, 339).

***m*-Bromo-iodo benzene** C_6H_4BrI [1:3]. (252°). Similarly prepared (K.).

***p* Bromo-iodo-benzene** C_6H_4BrI [1:4]. [92°]. (252°). Similarly prepared (Griess, *J.* 1866, 452; K.).

Dichloride C_6H_4BrI,Cl_2. [115°–120°, with decomposition]. Ppd. as yellow needles when chlorine is passed into a solution of bromo-iodo-benzene in chloroform (C. Willgerodt, *J. pr.* [2] 33, 158). With alcohol it forms aldehyde and C_6H_4BrI. It converts metallic and alcoholic iodides into chlorides, iodine being separated.

Tri-bromo-iodo-benzene $C_6H_2Br_3I$ [1:3:5:6]. [104°]. Obtained by adding conc. HI to a solution of $C_6H_2Br_3.N{:}N.NO_3$. Colourless needles, sol. hot alcohol (Silberstein, *J. pr.* [2] 27, 120).

Tri-bromo-iodo-benzene $C_6H_2IBr_3$ [1:2:4:5]. [165°].

Dichloride $C_6H_2IBr_3Cl_2$. Formed by dissolving $C_6H_2IBr_3$ in $CHCl_3$ and passing in Cl_2 (Willgerodt, *J. pr.* [2] 33, 159).

***s*-BROMO-IODO-ETHANE** C_2H_4BrI *i.e.* $CH_2Br.CH_2I$. *Ethylene bromiodide.* [28°]. (163°) S.G. [22] 2·516. From bromo-ethylene and conc HIAq at 100° (Reboul, *A.* 155, 2[illegible]); also from ethylene and BrI (Maxwell Simpson, *Pr.* 22, 51). Needles; sl. sol. cold alcohol. Alcoholic KOH gives iodo-ethylene and acetylene (Lagermark, *J. R.* 5, 334).

***u*-Bromo iodo-ethane** $CH_3.CHBrI$. *Ethylidene bromiodide.* (148°). S.G. [1?] 2·452. From bromo-ethylene and conc. HIAq at 4° (R.), or from *u*-di-iodo-ethane and IBr (Maxwell Simpson, *Pr.* 27, 421). Alcoholic KOH forms bromo-ethylene.

Di-bromo-iodo-ethane $C_2H_3IBr_2$. (170°–180°). S.G. [20] 2·86. From bromo-ethylene and IBr (M. Simpson, *Pr.* 22, 51). Ag_2O forms C_2H_3Br.

***s* - BROMO - IODO - ETHYLENE** C_2H_2IBr. *Acetylene bromiodide.* [c. 8°]. (150° cor.). S.G. (solid) [2] 2·750; [17·5] 2·627. Got by passing acetylene into aqueous solution of BrI, the product being treated with $Na_2S_2O_3$ and distilled with steam (Plimpton, *C. J.* 41, 395; Sabanejeff, *A.*

216, 266). With alcoholic NaOH it appears to give off C_2HBr.

u-Bromo-iodo-ethylene CH_2:CBrI. (129°). S.G. $\frac{9}{}$ 2·565. From chloro-bromo-iodo-ethane and alcoholic KOH (Henry, *C. R.* 98, 741). Slowly absorbs oxygen from air.

Di-bromo-iodo-ethylene CIBr:CHBr. [66°]. Small prisms. Formed by the action of an aqueous solution of bromine upon iodo-propiolic acid IC⋮C.CO_2H, CO_2 being evolved (Homolka a. Stolz, *B.* 18, 2285).

BROMO-IODO-METHANE CH_2BrI. *Methylene bromiodide.* (139°). S.G. $\frac{16.8}{16.8}$ 2·926. V.D. 9·65. From methylene iodide and Br or IBr (Henry, *C. R.* 101, 599).

Di-bromo-iodo-methane $CHBr_2I$. *Bromiodoform.* [6°]. From iodoform and Br (Serullas, *A. Ch.* [2] 34, 225; 39, 97; Bouchardat, *J. Ph.* 23, 10).

BROMO-IODO-NAPHTHALENES $C_{10}H_6BrI$. The three following are obtained from the corresponding bromo-naphthylamines by the diazo-reaction (Meldola, *C. J.* 47, 523):

(αα)-**Bromo-iodo-naphthalene** $C_{10}H_6BrI$ [1:4]. [84°]. Large flat needles; insol. water; sol. alcohol and glacial HOAc, v. e. sol. benzene and ether.

(αβ)-**Bromo-iodo-naphthalene** $C_{10}H_6BrI$ [1:3]. [68°]. Needles.

(αβ)-**Bromo-iodo-naphthalene** $C_{10}H_6BrI$ [1:2]. [94°]. Thick needles.

BROMO-IODO-NITRO-BENZENE $C_6H_3BrI(NO_2)$ [1:2:5]. [106°]. From C_6H_4BrI [1:2] and HNO_3 or from $C_6H_3Br(NH_2)(NO_2)$ [1:2:5] (Körner, *G.* 4, 383). Needles or prisms. Alcoholic NH_3 displaces I by NH_2.

Bromo-iodo-nitro-benzene $C_6H_3BrI(NO_2)$ [1:4:3]. [90°]. From $C_6H_3Br(NH_2)(NO_2)$ [1:4:3] (K.).

Bromo-iodo-nitro-benzene $C_6H_3BrI(NO_2)$ [1:3:4]. [84°]. From $C_6H_3Br(NH_2)(NO_2)$ [1:3:4] (K.). Alcoholic NH_3 displaces I by NH_2.

Bromo-iodo-nitro-benzene $C_6H_3BrI(NO_2)$ [1:3:6?]. [127°]. Formed, together with the following body, by dissolving *m*-bromo-iodo-benzene in fuming HNO_3 (K.). Alcoholic NH_3 displaces Br by NH_2.

Bromo-iodo-nitro-benzene $C_6H_3BrI(NO_2)$ [1:3:2?]. Needles.

BROMO-IODO-NITRO-PHENOL $C_6H_2(OH)(NO_2)BrI$ [1:2:4:6]. [104°]. From (1,3,4)-bromo-nitro-phenol, KOH, HIO_3, and I (Körner, *J.* 1867, 617). Monoclinic tables $a:b:c$ = ·520 : 1 : ·887; β = 65° 32′ (Groth, *Z. Kryst.* 1, 437); volatile with steam.—KA′.—NaA′.

Bromo-iodo-nitro-phenol $C_6H_2(OH)(NO_2)BrI$ [1:4:2:6]. From (1,3,6)-bromo-nitro-phenol as above (K.). Prisms (from ether).—KA′: yellow needles.

BROMO-IODO-NITRO-TOLUENE $C_6H_2MeBrI(NO_2)$ [1:3:4:*x*]. [118°]. Formed by nitrating (1,3,6)-bromo-iodo-toluene. Needles (Wroblewsky, *A.* 168, 160).

Bromo-iodo-nitro-toluene $C_6H_2MeBrI(NO_2)$ [1:3:2 or 6:*x*]. From the corresponding bromo-iodo-toluene (W.).

Di-bromo-iodo-nitro-toluene $C_6HMeBr_2I(NO_2)$ [1:3:5:4:2]. [69°]. From $C_6H_2MeBr_2I$ by nitration (Wroblewsky, *A.* 192, 210). Large needles. Volatile with steam.

Di-bromo-di-iodo-nitro-toluene $C_6MeBr_2I_2(NO_2)$ [1:3:5:4:2:6]. [129°]. From $C_6HMeBr_2I_2$ and fuming HNO_3. Yields on reduction by Sn and HCl an amido- compound which is converted by further treatment by Sn and HCl to *o*-toluidine (W.).

BROMO-DI-IODO-PHLOROGLUCIN $C_6(OH)_3BrI_2$. From tri-bromo-phloroglucin and aqueous KI. Decomposed by heat (Benedikt a. Schmidt, *M.* 4, 605).

BROMO-IODO-PROPANE C_3H_6BrI *i.e.* CH_3.CBrI.CH_3. (148°). S.G. $\frac{11}{}$ 2·20. Formed by union of HI with allylene hydrobromide (Reboul, *C. R.* 74, 669, 944).

Bromo-iodo-propane CH_3.CHI.CH_2Br or CH_3.CHBr.CH_2I. (160°–168°). From propylene, water, and IBr (M. Simpson, *Pr.* 22, 51).

DI-BROMO-IODO-PROPYLENE $C_3H_3IBr_2$ (?). From iodo-allylene and Br. Does not combine with Br (Liebermann, *A.* 135, 275).

DI-BROMO-IODO-STEARIC ACID $C_{18}H_{33}Br_2IO_2$. From ricinoleïc acid $C_{18}H_{34}O_3$ *viâ* $C_{18}H_{33}IO_2$ (Claus, *B.* 9, 1917).

BROMO-IODO-TOLUENE C_6H_3MeBrI [1:2:3 or 5]. (260°). S.G. $\frac{18}{}$ 2·139. From $C_6H_3MeBr(NH_2)$ (Wroblewsky, *A.* 168, 164).

Bromo-iodo-toluene C_6H_3MeBrI [1:3:4]. (265°). S.G. $\frac{20}{}$ 2·014. From the corresponding bromo-toluidine (W.).

Di-bromo-iodo-toluene $C_6H_2MeBr_2I$ [1:3:5:4]. [86°]. (270°). From $C_6H_2MeBr(NO_2)(NH_2)$ *viâ* $C_6H_2MeBr(NO_2)I$, and $C_6H_2MeBr(NH_2)I$ (Wroblewsky, *A.* 192, 209). Also from di-bromo-*p*-toluidine, $C_6H_2MeBr_2(NH_2)$ by diazo- reaction.

Di-bromo-di-iodo-toluene $C_6HMeBr_2I_2$ [1:3:5:4:2]. [68°]. From $C_6HMeBr_2I(NH_2)$ by diazo- reaction (Wroblewsky, *A.* 192, 212).

DI-BROMO-IODO-TOLUIDINE $C_6HMeBr_2I(NH_2)$ [1:3:5:4:2]. [64°]. By reduction of the corresponding nitro- compound (Wroblewsky, *A.* 192, 210). Converted by sodium amalgam into *o*-toluidine.

Acetyl derivative $C_6HMeBr_2I(NHAc)$ [121°]. Small white needles.

BROMO-ISATIC ACID *v.* ISATIC ACID.

BROMO-ISATIN *v.* ISATIN.

BROMO-ISATOÏC ACID *v.* ISATOÏC ACID.

BROMO-ISO- *v.* BROMO-.

BROMO-ITACONIC ACID $C_5H_5BrO_4$. [164°]. Formed by the dry distillation of *ita*-di-bromo-pyrotartaric acid (Swarts, *J.* 1873, 584). Its anhydride is formed similarly from *ita*-di-bromo-pyrotartaric anhydride (Petri, *B.* 14, 1637). Alkalis form aconic acid; Sn reduces it to itaconic acid.

BROMO-LACTIC ACID *v.* BROMO-OXY-PROPIONIC ACID.

DI-BROMO-LAURENE $C_{11}H_{12}Br_2$ (?) [210°]. From laurene and Br (Montgolfier, *A. Ch.* [5] 14, 93).

Tri-bromo-laurene $C_{11}H_{13}Br_3$? [125°]. From laurene and Br in the cold (Fittig, Köbrich a. Jilke, *A.* 145, 149). *Cf.* LAURENE.

BROMO-LEVULIC ACID *v.* BROMO-ACETYL-PROPIONIC ACID.

BROMO-LUTIDINE *v.* BROMO-DI-METHYL-PYRIDINE.

BROMO-MALEÏC ACID $C_2HBr(CO_2H)_2$ *i.e.* CO_2H.CH:CBr.CO_2H, or CO_2H.C.CHBr.CO_2H, or $\begin{array}{l}CBr.C(OH)_2 \\ \| \\ CH\ .\ CO\end{array}\!\!>\!O$, or $\begin{array}{l}CH.C(OH)_2 \\ \| \\ CBr\ .\ CO\end{array}\!\!>\!O$. [128°].

Formed by boiling di-bromo-succinic acid or its Ba salt with water (Kekulé, *A. Suppl.* 1, 367; Petri, *A.* 195, 62). Formed also, together with bromo-fumaric acid (*q. v.*) by the action of Br and water on succinic acid at 180° (Kekulé, *A.* 130, 1), or fumaric acid at 100° (Carius, *A.* 149, 264). Deliquescent prisms or needles; v. e. sol. water, alcohol, and ether. Splits up into water and its anhydride on distillation.

For discussion of formula see MALEIC ACID.

Reactions.—1. *Sodium-amalgam* gives succinic acid. 2. Fuming HBr unites in the cold, forming di-bromo-succinic acid. 3. *Electrolysis* of its Na salt gives CO and HBr. 4. Boiling conc. *baryta-water* forms oxalic and acetic acids.—5. When it is dissolved in water and an equivalent of aniline is added there separates a crystalline pp. $C_4HBr_2(CO_2H)(CO_2H.NH_2C_6H_5)$. [128°]. This acid aniline salt dissolved in water and allowed to stand deposits the acid anilide $CO_2H.C_2HBr.CO.NHC_6H_5$ which crystallises in prisms; insol. in dilute HCl. If instead of allowing the substance to react in the cold the solution is heated, the compounds $C_{16}H_{12}N_2O_2$ and $C_{16}H_{14}N_2O_4$ are obtained.

$C_{16}H_{12}N_2O_2$, probably $\begin{matrix} C(NHPh)\cdot CO \\ \| \\ CH\text{———}CO \end{matrix}\!\!>\!NPh$, [230°], forms ochre-coloured microscopic needles. Insol. hot, sl. sol. cold aq; sol. hot alcohol, less in cold; $C_{16}H_{14}N_2O_4$, probably $\begin{matrix} C(NHPh)\ \ CO_2H \\ \| \\ CH.CO.NHPh \end{matrix}$, [175°], forms yellowish indistinct crystals. Sol. hot, m. sol. cold aq. Sol. alkalis: acids pp. the substance unchanged (Michael, *Am.* 9, 180; *B.* 19, 1373).

Salts. Ag_2A'': crystalline pp. CaA'' 2aq. —$CaNa_2A''_2$ 4aq. PbA''aq.

Dimethyl ether $A''Me_2$. (238° i.V.). Converted by iodine into dimethyl bromo fumarate.

Diethyl ether $A''Et_2$. (256 i.V.). (140°–150°) at 25 mm. (Anschütz, *B.* 12, 2284; Schacherl, *A.* 229, 91).

Anhydride C_4HBrO_3. (215° i.V.). Formed as above, and also by heating di-bromo-succinic acid with Ac_2O at 130° (Anschütz, *B.* 10, 1881). Water forms bromo-maleic acid.

Amide $C_4H_4BrN_2O_2$. [168°–175°]. From the imide and NH_3.

Imide $(C_4HBrO_2)NH$. [151°]. Formed, together with the amide of di-bromo-maleic acid, by heating succinimide with Br at 160° (Ciamician a. Silber, *B.* 17, 557; Kreichmski, *Sitz. B.* 71, 561).

Iso-bromo-maleic acid is BROMO-FUMARIC ACID (*q. v.*).

Bromo-maleic acid (?) $C_4H_3BrO_4$. [112°]. From mucobromic acid and baryta (Hill, *B.* 17, 239).- K_2A''aq.- BaA'' 2aq. Ag_2A''.

Di-bromo-maleic acid $C_4Br_2H_2O_4$. [123°]. Formed, together with bromo-fumaric acid, by brominating succinic acid (Kekulé, *A.* 130, 2). From ($\beta\gamma$)-di-bromo-pyromucic acid and from tri-bromo-pyromucic acid by hot dilute HNO_3 (Hill a. Sanger, *A.* 232, 89). Formed also by heating mucobromic acid with Br at 140° (Hill, *Am.* 3, 48; *B.* 13, 734). Slender felted needles, v. sol. water, alcohol, and ether, v. sl. sol. benzene and ligroïn. An equivalent quantity of aniline added to a solution of the acid in water dissolves and then deposits the acid aniline salt. When this is allowed to stand under water it gradually forms an anilide. The neutral salt in the same way gives the di-anilide $C_2Br_2(CO.NHPh)_2$. [140°]. By heating the acid (3 pts.), with water (60 pts.) and aniline (2·2 pts.) for 30 minutes $\begin{matrix} C(NHPh)\cdot CO \\ \| \\ CBr\text{———}CO \end{matrix}\!\!>\!NPh$ [183°] is obtained in the form of flat, yellowish red prisms; insol. aq.; m. sol. hot alcohol (Michael, *Am.* 9, 180).

Salts. BaA'' 2aq. S. 6·5 at 20°. PbA''aq. —Ag_2A'': explodes when heated.

Anhydride $C_4Br_2O_3$. [115°]. Prepared by heating the acid. Needles (by sublimation); sl. sol. cold water.

Imide $\begin{matrix} CBr.CO \\ \| \\ CBr.CO \end{matrix}\!\!>\!NH$. [225°]. Formed by heating succinimide with bromine. Monoclinic crystals. $a:b:c$ = ·4342:1:·3649; β = 110° 49'. By boiling with aqueous KOH it is converted into di-bromo-maleic acid (Ciamician u. Silber, *B.* 17, 556; *G.* 14, 35; *cf.* Kreichmski, *Sitz. B.* 71, 561).

Bromo-maleic-acid-di-bromide *v.* TRI-BROMO-SUCCINIC ACID.

DI-BROMO-MALEIC ALDEHYDE $C_4H_2Br_2O_2$. [90°]. Got in small quantity from ($\beta\gamma$)-di-bromo-pyromucic acid and aqueous bromine (Tönnies, *B.* 12, 1203; Hill a. Sanger, *A.* 232, 87). Long thin prisms (from water). V. sol. alcohol, ether, chloroform, and benzene, m. sol. light petroleum. In a current of CO_2 it may be sublimed. On oxidation it gives mucobromic acid.

BROMO-MALEYL BROMIDE $C_4HBr_3O_2$. [56°]. Formed by treating (γδ) di-bromo-pyromucic acid with cold bromine (Hill a. Sanger, *A.* 232, 89). Long prisms (from light petroleum).

BROMO-MALIC ACID $C_4H_5BrO_5$. The sodium salt $NaHA''$ is formed by the action of NaOEt sodium di-bromo succinate. Boiling lime-water converts it into calcium racemate. Sodium-amalgam forms sodium succinate. $Pb(OAc)_2$ pps. PbA''.

Ethyl derivative. Sodium salt $CO_2Na.CH_2.CH(OEt).CO_2Na$. Hygroscopic mass; formed by adding alcoholic NaOEt to sodium di-bromo succinate (Mulder a. Hamburger, *R. T. C.* 1, 151).

BROMO-MALONIC ACID $C_3H_3BrO_4$ *i.e.* $CHBr(CO_2H)_2$. Obtained by reducing the di-brominated acid with sodium amalgam (Petrieff, *J. R.* 10, 65; *B.* 11, 415). Deliquescent; moist Ag_2O forms tartronic acid. $AgHA''$. Ag_2A''.

Di-bromo-malonic acid $CBr_2(CO_2H)_2$ [c. 126°]. From malonic acid $CHCl_3$ and Br (Petrieff, *B.* 7, 400; *J. R.* 10, 65; Van 't Hoff, *B.* 8, 355). Needles, v. e. sol. water. Boiling baryta water forms oxalic acid.

Amide $CBr_2(CONH_2)_2$. [206°]. Formed by adding Br to malonamide in aqueous solution (Freund, *B.* 17, 782). Formed also by the action of alcoholic NH_3 on the amide of penta-bromo-aceto-acetic acid $CBr_3.CO.CBr_2.CO.NH_2$ (Stokes a. Pechmann, *Am.* 8, 380). Needles, prisms, or large octahedra. Sl. sol. hot water, alcohol, and acetic acid. - $CBr_2\!\!<\!\begin{matrix} CO.NH \\ CO.NH \end{matrix}\!\!>\!Hg$: white amorphous powder, insoluble in water and alcohol.

Methylamide $CBr_2(CO.NHMe)_2$: [162°];

large white needles or trimetric crystals (Freund, *B.* 17, 782).

BROMO-MALOPHTHALIC ACID $C_8H_{11}BrO_5$. From tetra-hydro-phthalic acid and bromine-water (Baeyer, *A.* 166, 353). Prisms or tables (containing ½aq). Baryta-water converts it into $C_8H_{12}O_6$.

BROMO-MELILOTIC ACID *v.* Bromo-oxy-phenyl-propionic acid.

BROMO-MESITENE LACTONE $C_6H_4Br<^{O}_{CO}>$. [105°]. From mesitene lactone, CS_2 and Br (*v.* Aceto-acetic ether). Sl. sol. cold alcohol and water (Hantzsch, *A.* 222, 18).

BROMO-MESITOL $C_9H_{11}BrO$ *i.e.* $C_6HMe_3Br(OH)$. [80°]. Needles (from alcohol) (Biedermann a. Ledoux, *B.* 8, 59).

Di-bromo-mesitol $C_6Me_3Br_2(OH)$. [150°]. From mesitol, Br, HOAc, and I (Jacobsen, *A.* 195, 265).

BROMO MESITYL ALCOHOL *v.* Bromo-ω-oxy-mesitylene.

p-**BROMO-MESITYL BROMIDE** *v.* *p*-ω-Di-bromo-mesitylene.

BROMO-MESITYLENE $C_6H_2Me_3Br$ [1:3:5:4]. *Bromo-s-tri-methyl-benzene.* [−1°]. (227° i. V.). S.G. ¹⁰ 1·32. Formed by the action of 1 mol. Br upon cold mesitylene in the dark (Fittig a. Storer, *A.* 147, 6; Schramm, *B.* 19, 212).

(5:3:1) ω-**Bromo-mesitylene** $C_6H_3(CH_3)(CH_2Br)$ [1:3:5]. *Mesityl bromide.* [38°]. (231°). Prisms. Formed by bromination of mesitylene at 130° (Wispek, *B.* 16, 1577; Colson, *A. Ch.* [6] 6, 89; *C. R.* 96, 713).

eso **Di-bromo-mesitylene** $C_6HMe_3Br_2$. [61°]. (278°). Long needles. Formed by the action of 2 mols. of bromine upon mesitylene in the dark (F. a. S.; Süssenguth, *A.* 215, 248; Schramm, *B.* 19, 212). Fuming HNO_3 gives bromo-di-nitro mesitylene [194°].

p-ω-**Di-bromo-mesitylene** $C_6H_2(CH_3)_2Br(CH_2Br)$ [5:3:4:1]. *p-Bromo-mesityl bromide.* Oil, fluid at −19°. Decomposes on distillation. Formed by the action of bromine (1 mol.) in *sunshine* upon *eso*-bromo-mesitylene (Schramm, *B.* 19, 213).

ωω-**Di-bromo mesitylene** $C_6H_3Me(CH_2Br)_2$. [66°]. Formed by passing CO_2 charged with bromine vapour into boiling mesitylene (Colson, *A. Ch.* [6] 6, 92; *C. R.* 96, 713; Robinet, *C. R.* 96, 500). Formed also by treating ωω-di-oxy-mesitylene with HBr (Robinet a. Colson, *Bl.* [2] 40, 111). Long prisms; decomposed by alcohol.

Tri-*eso*-bromo-mesitylene $C_6Me_3Br_3$. [224°]. Formed by the action of 3 mols. of bromine upon mesitylene in the dark (Schramm, *B.* 19, 213). Triclinic crystals, v. sl. sol. alcohol.

i $\omega_1\omega_2$-**Tri-bromo-mesitylene** $C_6H_2(CH_3)Br(CH_2Br)_2$ [5:4:3:1]. [122°]. Obtained by the action of bromine (1 mol.) in *sunshine* upon hot *p*-ω-di-bromo mesitylene (*p*-bromo-mesityl-bromide) $C_6H_2(CH_3)_2Br(CH_2Br)$. Very slender needles (from alcohol) Schramm, *B.* 19, 215).

c-$\omega_1\omega_2$-**Tri-bromo mesitylene** $C_6H_2MeBr(CH_2Br)_2$ [5:2:1:3]. [81°]. From bromo $\omega_1\omega_2$-di-oxy-mesitylene and conc. HBr. Can be formed by brominating mesitylene (Colson, *A. Ch.* [6] 6, 101; *Bl.* [2] 41, 362).

$\omega_1\omega_2\omega_3$ **Tri-bromo-mesitylene** $C_6H_3(CH_2Br)_3$. [94°]. (21?°) at 10 mm. From boiling mesitylene and Br (3 mols.). Needles, v. sol. boiling alcohol (Colson, *C. R.* 96, 713; *A. Ch.* [6] 6, 96).

BROMO-MESITYLENE GLYCOL *v.* Bromo-di-oxy-mesitylene.

BROMO-MESITYLENE SULPHONIC ACID $C_9H_{11}BrSO_3$ *i.e.* $C_6HMe_3Br.SO_3H$. Formed by the action of bromine-water on a very dilute solution of mesitylene-sulphonic acid or its Ba salt; formed also from bromo-mesitylene and fuming H_2SO_4 (Rose, *A.* 164, 56). Deliquescent trimetric needles (from ether).—BaA'_2 aq.—PbA'_2 1½aq. KA'aq. CuA'_2 4aq. NaA'.

(α)-**BROMO-MESITYLENIC ACID** $C_9H_9BrO_2$ *i.e.* $C_6H_2Me_2Br(CO_2H)$ [1:3:4:5]. [147°]. Formed, together with some of its isomerides, by the slow action of Br on mesitylenic acid in the cold. Formed also from the corresponding amido-mesitylenic acid (Schmitz, *A.* 193, 172). Trimetric prisms (from alcohol), $a:b:c$ = ·927:1:·470.—BaA'_2 4aq: monoclinic, $a:b:c$ = 3·068:1:·801; β = 63° 24'.—CaA'_2 2aq.

(β)-**Bromo-mesitylenic acid** $C_6H_2Me_2Br(CO_2H)$ [1:3:2:5]. [215°] (Sch.); [212°] (S.). Formed by oxidising bromo-mesitylene (Fittig a. Storer, *A.* 147, 1), or from the corresponding amido-acid (Sch.). Monoclinic crystals, $a:b:c$ 1·193:1:·760; β = 70° 35'.—BaA'_2.—CaA'_2. CaA'_2 5aq. KA'.

Di-bromo-mesitylenic acid $C_6HBr_2Me_2(CO_2H)$. [195°]. Formed by oxidising di-bromo-mesitylene (Süssenguth, *A.* 215, 250). Needles (by sublimation).—CaA'_2 7aq.—BaA'_2 3½aq.

BROMO-METHACRYLIC ACID $C_4H_5BrO_2$ *i.e.* $CHBr:CMe.CO_2H$. *Bromo-crotonic acid.* [63°]. (229°). From *citra-* or *mesa-* di-bromo-pyrotartaric acid by treatment with water, Na_2CO_3Aq, or KOHAq (Kekulé, *A. Suppl.* 2, 97; Cahours, *A. Suppl.* 2, 347; Fittig a. Krusemark, *A.* 206, 7; Friedrich, *A.* 203, 354). Also from αβ-di-bromo-isobutyric acid and NaOHAq (C. Kolbe, *J. pr.* [2] 25, 382). Flat needles, sl. sol. cold water. Reduced by sodium-amalgam to isobutyric acid. Decomposed by heating with alkalis into methane, allylene, and acetic acid (F.).—CaA'_2 3aq. S. (of CaA'_2) 5·75 at 11°.—AgA'.—$HO.CuA'$. $NH_4HA'_2$ (Morawski, *Sitz. B.* 74, 39).

Ethyl ether EtA'. (193°) (C.).

Bromo-methacrylic acid $CH_2:C(CH_2Br).CO_2H$. [66°]. Formed, together with the preceding, by boiling *mesa*-di-bromo-pyrotartaric acid with water or Na_2CO_3Aq (Krusemark, *A.* 206, 12). Laminæ (from water), v. sol. water; volatile with steam. Reduced with difficulty by sodium-amalgam to isobutyric acid.—CaA'_2 2aq. S. (of CaA'_2) 80 at 5°.

Di-bromo-methacrylic acid $C_4H_4Br_2O_2$. Needles. From tri-bromo-butyric acid (dibromide of bromo-methacrylic acid). At 120° it takes up Br forming tetra-bromo-butyric acid, whence boiling alkalis form

Tri-bromo-methacrylic acid $C_4H_3Br_3O_2$. Needles (C.).

BROMO-METHANE *v.* Methyl bromide.

Di-bromo-methane *v.* Methylene bromide.

Tri-bromo-methane *v.* Bromoform.

Tetra-bromo-methane CBr_4. *Carbon tetrabromide.* [92°]. (189°). Occurs in commercial bromine (Hamilton, *C. J.* 39, 48).

Formation.—1. By heating Br with CS_2 in presence of I or $SbBr_3$ (Bolas a. Groves, *C. J.* 23, 161; 24, 773; *A.* 156, 60; 160, 160).—2.

From CH_2Cl_2 and IBr_3 (Höland, *A.* 240, 236).—3. From alcohol and Br (Schäffer, *B.* 4, 366).—4. By exposing a mixture of dilute KOH, bromoform, and Br to sunlight (Habermann, *A.* 167, 174).—5. By heating bromoform or bromopicrin with $SbBr_3$ or BrI at 150°.—6. From CI_4 and Br (Gustavson, *A.* 172, 176).—7. From CCl_4 and Al_2Br_6 at 100° (Gustavson, *J. R.* 13, 286). 8. From CH_3Br and Br in presence of animal charcoal (Damoiseau, *C. R.* 92, 42).

Preparation.—CS_2 (2 pts.) is heated with iodine (3 pts.) and Br (14 pts.) for 96 hours at 150° (Höland, *A.* 240, 238).

Properties. Tables with faint camphor like smell; extremely prone to sublimation. At 220° it splits up into C_2Br_4 and bromine. Boiling alcohol gives bromal, HBr, and aldehyde. Alcoholic KOH gives K_2CO_3 and KBr. Sodium-amalgam forms $CHBr_3$ and CH_2Br_2.

BROMO METHANE DI-SULPHONIC ACID $CHBr(SO_3H)_2$. Potassium salt K_2A''. From bromo-di-sulpho-aldehyde $CBr(SO_3H)_2.CHO$ by boiling with aqueous K_2CO_3 (Rathke, *A.* 161, 161).

Di bromo methane sulphonic acid $CHBr_2.SO_3H$. Barium salt BaA'_2. Thin unctuous plates, formed by the action of Br upon barium sulpho-acetate at 130° (Andreasch, *M.* 7, 157).

BROMO PENTA-METHYL-TRI-AMIDO TRI-PHENYL-CARBINOL $C_{24}H_{30}BrN_3O$. Hydrobromide $C_{24}H_{28}N_3 3HBr$. Formed by heating di-methyl-aniline with Br at 120° (Brandenburg a. Brunner, *B.* 10, 1845, 11, 697).

DI-BROMO-METHYLAMINE $MeNBr_2$ *v.* METHYLAMINE.

p-**BROMO-METHYL-ANILINE** $C_6H_4(Br)NHMe$. [11°]. (260°). Prepared from the nitrosamine.

Acetyl derivative [90°].

Nitrosamine $C_6H_4(Br)NMe(NO)$. [71°]. Long needles. Formed by the action of HNO_2 on *p*-bromo-di-methyl-aniline (Wurster a. Scheibe, *B.* 12, 1818).

m-**Bromo-di-methyl-aniline** $C_6H_4(Br)NMe_2$ [1:3]. [11°]. (264° corr.). Prepared by the methylation of *m*-br-aniline. By the action of HNO_2 it gives a nitroso compound which forms light green needles and melts at about 148°.

Methylo-iodide $C_6H_4Br.NMe_3I$. [201°]. Leaflets (Wurster a. Scheibe, *B.* 12, 1818).

p-**Bromo-di-methyl-aniline** $C_6H_4(Br)NMe_2$ [1:4]. [55°]. (264° corr.).

Preparation. 1. By bromination of di-methyl-aniline dissolved in acetic acid (Weber, *B.* 8, 714; 10, 763). 2. By methylation of *p*-brom-aniline. By the action of HNO_2 it gives a mixture of *p*-nitro-di-methyl-aniline and *p*-bromo-phenyl-methyl-nitrosamine.

Methylo-iodide $C_6H_4Br.NMe_3I$. [185°] (Wurster a. Scheibe, *B.* 12, 1816).

Ferrocyanide $B'_4H_4Fe(CN)_6 2aq$: leaflets.

Ferricyanide $B'_6H_6Fe_2(CN)_{12}$ 5aq: very soluble yellow crystals (Wurster a. Roser, *B.* 12, 1825).

BROMO-DI-METHYL-ANILINE-PHTHALEIN $C_{24}H_{22}Br_2N_2O_2$ *i.e.*

$$C_6H_4<\begin{matrix}C(C_6H_3BrNMe_2)_2\\CO.O\end{matrix}>.$$

The hydrochloride, formed by heating *p*-bromo-di-methyl-aniline with phthalyl chloride, crystallises in steel-blue needles. Conc. HClAq pps. dingy-green B"2HCl (O. Fischer, *B.* 10, 1623).—$B''_2H_2PtCl_6$.

DI-BROMO-METHYL-ANTHRACENE $C_{15}H_{10}Br_2$. [138°-140°]. From methyl-anthracene by Br in CS_2 (Liebermann, *A.* 212, 85). Yellow needles (from glacial HOAc).

Tetra-bromo-methyl-anthracene $C_{15}H_8Br_4$. Needles (from toluene). Oxidises to di-bromo-methyl-anthraquinone (L.).

DI-BROMO-DI-METHYL-ANTHRACENE DIHYDRIDE $C_{16}H_{14}Br_2$. From di-methyl-anthracene dihydride and Br in HOAc (Anschütz, *A.* 235, 309). Oxidises to anthraquinone.

DI-BROMO METHYL-ATROLACTIC ACID *v.* DI-BROMO-OXY-TOLYL-PROPIONIC ACID.

TETRA BROMO METHYL-AURINE $C_{20}H_{12}Br_4O_3$. Formed by brominating methyl-aurine. B'HBr 2aq (Zulkowsky, *M.* 3, 471).

BROMO-METHYL-BENZENE *v.* BROMO-TOLUENE.

Bromo-di-methyl-benzene *v.* BROMO-XYLENE.

Tri-bromo-tri-methyl-benzene $C_6(CH_3)_3Br_3$ [1:2:3:4:5:6]. *Tri bromo hemimellithene.* [245°]. Needles. Sl. sol. alcohol. Formed by bromination of (1.2:3)-tri-methyl-benzene (Jacobsen, *B.* 15, 1858). Other bromo-tri-methyl-benzenes are described as BROMO-ψ-CUMENES and BROMO MESITYLENES.

Bromo-tetra-methyl-benzene *v.* BROMO DURENE.

Bromo-penta-methyl-benzene C_6BrMe_5 [161°]. (289°). From C_6Me_5H, Br, and I (Friedel a. Crafts, *A. Ch.* [6] 1, 473).

Hexa-ω-bromo-hexa-methyl-benzene $C_6(CH_2Br)_6$. [255°] (F. a. C.); [227°] (H.). From hexa-methyl-benzene, water, and Br at 100° (Hofmann, *B.* 13, 1732; Friedel a. Crafts, *A. Ch.* [6] 1, 468).

BROMO-METHYL-BENZOIC ACID *v.* BROMO-TOLUIC ACID.

Bromo-di-methyl-benzoic acid $C_6H_2BrMe_2CO_2H$. [173°]. *Bromo-pseudo-cumenic acid. Bromo-xylylic acid.* From $C_6H_2BrMe_3$ [1:2:4:5] by CrO_3 in HOAc (Süssenguth, *A.* 215, 246). Also from $C_6H_3Me_2(CO_2H)$ [1:3:4] and Br (Gunter, *B.* 17, 1608). Needles (from water). V. e. sol. alcohol.—CaA'_2 2aq. BaA'_2 6aq.

Bromo-di-methyl-benzoic acid $C_6H_2BrMe_2CO_2H$. [189°]. *Bromo-p-xylylic acid.* From $C_6H_3Me_2(CO_2H)$ [1:2:4] and Br (Gunter, *B.* 17, 1609). Needles (from dilute alcohol).

Other isomerides are described as BROMO-MESITYLENIC ACIDS (*q. v.*).

exo-**BROMO-DI METHYL-COUMARIN**

$$C_6H_3(CH_3)<\begin{matrix}C(CH_3):CBr\\|\\O\text{——}CO\end{matrix}.$$

Formed by bromination of di-methyl-coumarin dissolved in CS_2. Crystalline solid. Sl. sol. alcohol. Converted by hot alcoholic KOH into di-methyl-coumarilic acid (di-methyl-coumarone-carboxylic acid) (Hantzsch a. Lang, *B.* 19, 1299).

DI-BROMO-METHYLENE-DI-PHENYLENE $C_{13}H_8Br_2$ [192°]. From methylene-di-phenylene (*q. v.*). Needles or octahedra (from ether) (Carnelley, *C. J.* 37, 710).

HEXA-BROMO-METHYLENE-DI-PHENYLENE OXIDE $C_{13}H_4Br_6O$. Formed, together with the hepta-brominated compound $C_{13}H_3Br_7O$ [136°], by adding Br to *o*-methylene-di-phenylene oxide suspended in water. Blackens at c. 225° (Salzmann a. Wichelhaus, *B.* 19, 1401).

BROMO-METHYLENE-PHTHALIDE $C_9H_5BrO_2$ *i.e.* $C_6H_4\left<\begin{matrix}C{=}CHBr\\ >O\\ C{=}O\end{matrix}\right.$. [133°]. Long colourless needles. Formed by heating phthalyl-bromo-acetic acid *in vacuo*; or by bromination of acetophenone-carboxylic acid. It combines with Br_2 forming $C_6H_4<\begin{matrix}CBr(CBr_2H)\\ CO\end{matrix}>O$. [118°] (Gabriel, *B.* 17, 2525).

p-**BROMO-METHYL-ETHYL-ANILINE** $C_9H_{12}BrN$ *i.e.* $C_6H_4Br.NMeEt$. (265°). From methyl-ethyl-aniline and Br. Solidifies below 0° (Claus a. Howitz, *B.* 17, 1327).

TRI-BROMO-DI-METHYL-ETHYL-BENZENE $C_{10}H_{11}Br_3$ *i.e.* $C_6Br_3Me_2Et$. [218°]. (Jacobsen, *B.* 7, 1434).

DI-BROMO-METHYL-ETHYL-GLYOXALINE $C_3Br_2(CH_3)(C_2H_5)N_2$. *Di-bromo-oxal-ethyline.* [38°]. Colourless crystals. Sol. acids. Formed by bromination of methyl-ethyl-glyoxaline (oxal-ethyline) (Wallach, *B.* 16, 537).

HEXA-BROMO-METHYL-ETHYL-KETONE $C_4H_2Br_6O$ *i.e.* $CBr_3.CO.CH_2.CBr_3$. [90°]. From *u*-di-bromo-ethylene and HBrO (Demole, *B.* 11, 1710). Reduced by sodium-amalgam to methyl ethyl ketone. Fuming HNO_3 gives malonic acid.

DI-BROMO-(*B.* 2-*Py.* 2)-DI-METHYL-(*Py.* 3)-ETHYL-QUINOLINE $C_{13}H_{13}Br_2N$. [144°]. White needles (Harz, *B.* 18, 3389).

TRI-BROMO-METHYL-GLYOXALINE $C_3Br_3(CH_3)N_2$. *Tri-bromo-oxalmethylin.* [89°]. White crystals. Insoluble in cold water.

Formation.—1. By the action of MeI on tri-bromo-glyoxaline-silver.—2. By bromination of methyl-glyoxaline (oxal-methyline) dissolved in dilute H_2SO_4 (Wallach, *B.* 16, 537).

BROMO-METHYL-INDONAPHTHENE-CARBOXYLIC ACID $C_6H_4<\begin{matrix}CBrMe\\ CH\end{matrix}>C.CO_2H$. [215°]. Formed by bromination of methyl-indonaphthene in chloroform. Needles. Sl. sol. alcohol (Roser, *B.* 20, 1575).

HEXA-BROMO-DI-METHYL-METHYLENE DIKETONE $C_5H_2Br_6O_2$ *i.e.* $CBr_3.CO.CH_2.CO.CBr_3$. *Hexa-bromo-acetyl-acetone.* [108°]. From the diketone and Br (Combes, *A. Ch.* [6] 12, 210). Needles; decomposed by alkalis into tri-bromo-mesity...ne and tri-bromo-acetic acid.

...O-α-METHYL-NAPHTHALENE

eso-**Bro...** $C_{10}H_6Br(CH_3)$. (298° corr.). Colourless fluid. Formed by the ...action of bromine on a cold solution of (α)-methyl-naphthalene in CS_2.

Picric acid comp...ound $C_{11}H_9Br,C_6H_2(NO_2)_3OH$. [..95°]. Yellow needles (Schulze, *B.* 17, 1528).

eso-**Bromo-β-methyl-naphthalene** $C_{10}H_6Br(CH_3)$. (296°). Colourless fluid. Formed by the action of bromine on a cold solution of (β)-methyl-naphthalene in CS_2.

Picric acid compound $C_{11}H_9Br,C_6H_2(NO_2)_3OH$ [113°], yellow needles (Schulze, *B.* 17, 1528).

ω-**Bromo-(β)-methyl-naphthalene** $C_{10}H_7.CH_2Br$. [56°]. (213° at 100 mm.). White glistening plates. Formed by passing gaseous bromine into (β)-methyl-naphthalene heated to 240° (Schulze, *B.* 17, 1529).

Tri-bromo-di-methyl-naphthalene $C_{12}H_9Br_3$. [228°] (Cannizzaro a. Carnelutti, *G.* 12, 410; *cf.* Giovanozzi, *G.* 12, 147).

TRI-BROMO-METHYL-DI-PHENYL-AMINE $C_{13}H_{10}Br_3N$ *i.e.* $NMe(C_6H_3Br_2)(C_6H_4Br)$. [98°]. From methyl-di-phenyl-amine and Br (Gnehm, *B.* 8, 926). HNO_3 forms $\{C_6H_2Br(NO_2)_2\}_2NH$.

Tetra-bromo-methyl-di-phenyl-amine $(C_6H_3Br_2)_2NMe$. [129°]. Formed at the same time as the preceding (G.).

DI-BROMO-DI-METHYL-QUINOL *v.* *Di-methyl-* BROMO-HYDROQUINONE.

BROMO-METHYL-PIPERIDINE $CH_2<\begin{matrix}CHBr.CH_2\\ CH_2.CH_2\end{matrix}>NMe$. The methylo-bromide (B'MeBr) is formed very readily by isomeric change of di-methyl-εδ-di-bromo-*n*-amyl-amine (so-called 'di-methyl-piperidine-di-bromine'), $CH_2Br.CHBr.CH_2.CH_2.CH_2.NMe_2$, by warming its alcoholic solution for a short time (Merling, *B.* 19, 2630).

DI-BROMO-METHYL-PYRIDINE $C_6H_5Br_2N$ *i.e.* $C_5NH_2MeBr_2$. [109°]. Formed, together with ethylene bromide, from tropidine (*q. v.*) hydro-bromide and bromine at 165° (Ladenburg, *A.* 217, 145).

s-**Di-bromo-di-methyl-pyridine** $C_5NHMe_2Br_2$ [1:5:2:4]. *Di-bromo-lutidine.* [65°]. Formed by the action of bromine upon an aqueous solution of the potassium salt of *s*-di-methyl-pyridine-di-carboxylic acid. — $B'_2H_2Cl_2PtCl_4$ 2aq: needles (Pfeiffer, *B.* 20, 1350).

Di-bromo-*s*-tri-methyl-pyridine $C_5NMe_3Br_2$ [1:3:5:2:4]. *Di-bromo-collidine.* [81°]. (262°) at 726 mm. Obtained by the action of bromine upon an aqueous solution of the potassium salt of *s*-tri-methyl-pyridine-di-carboxylic acid; the yield is 50 p.c. of the theoretical. White pearly plates. Very volatile with steam. Weak base.

S a l t s.—B'HCl: easily soluble small glistening crystals. $B'_2H_2Cl_2PtCl_4$ 2aq: orange-yellow needles. $B'_2H_2Cr_2O_7$: [146°]; needles.—$B'C_6H_2(NO_2)_3OH$: [160°] dark-yellow flat prisms, v. sol. hot alcohol, insol. water (Pfeiffer, *B.* 20, 1345).

DI-BROMO-TRI-METHYL-PYRIDINE DI-CARBOXYLIC ETHER. *D i b r o m i d e* $NC_8H_7Br_2(CO_2Et)_2Br_2$. [102°]. From the following body and fuming HNO_3 (Hantzsch, *A.* 215, 17).

Di-bromo-tri-methyl-pyridine di-carboxylic ether. *D i - b r o m h y d r i d e* $NC_8H_7Br_2(CO_2Et)_2H_2Br_2$. [88°]. From the di-hydride of (1,3,5,2,4)-tri-methyl-pyridine-di-carboxylic ether by Br in CS_2 (Hantzsch, *A.* 215, 14). Yellow twin crystals.

DI-BROMO-DI-METHYL-PYROCATECHIN *v.* *Di-methyl ether* of DI-BROMO-PYROCATECHIN.

HEXA-BROMO-DI-METHYL TRISULPHIDE $C_2Br_6S_3$ *i.e.* $(CBr_3)_2S_3$. *Carbotrithiohexabromide.* [125°]. S. (alcohol) 5·5 at 78°; S. (ether) 2·35 at 0°. From CS_2 and Br (Hell a. Urech, *B.* 15, 275, 987; 16, 1147). Prisms or tables, insol. water. Hot conc. NaOH gives NaBr, Na_2CO_3, and Na_2S_3. Decomposed by heat into CBr_4, CS_2Br_4, SBr_2, and a blue substance $C_9Br_4S_4$ 2aq.

DI-BROMO-METHYL-THIOPHENE ...$HBr_2(CH_3)S$. (228°). Oil (Meyer a. Kreis, *B.* ...787).

T...i-bromo-(α)-methyl-thiophene $C_4Br_3(CH_3)S$. *Tri-b...mo-(β)-thiotolene.* [86°]. Formed by bromination of (β)-methyl-thiophene (Egli, *B.* 18,

545). Long colourless silky needles. V. sol. ether and hot alcohol.

Tri-bromo-methyl-thiophene $C_4Br_3(CH_3)S$. [39°]. Formed by bromination of the methyl-thiophene from pyrotartaric acid. Large colourless needles (Volhard a. Erdmann, *B.* 18, 455). Forms a molecular compound [74°] with the preceding (Gattermann, *B.* 18, 3005).

Bromo-di-methyl-thiophene $C_4H(CH_3)_2BrS$. *Bromo-thioxene*. (194° uncor.). Formed by bromination of thioxene dissolved in CS_2. Volatile with steam. Colourless fluid. Heavier than water (Messinger, *B.* 18, 1637).

Di-bromo-di-methyl-thiophene $C_4(CH_3)_2Br_2S$. *Di-bromo-thioxene*. [46°]. (247° uncor.). Long colourless needles. Formed by adding 2 mols. of bromine to cooled thioxene (from coal-tar) (Messinger, *B.* 18, 563).

Di-bromo-di-methyl-thiophene $C_4(CH_3)_2Br_2S$. *Di-bromo-thioxene*. [47°-50°]. Needles. Volatile with steam. Formed by bromination (with $2Br_2$) of thioxene (from acetonyl-acetone) (Paal, *B.* 18, 2253).

Tri-bromo-di-methyl-thiophene $C_6H_5Br_3S$ *i.e.* $C_4Br_2(CH_3)(CH_2Br)S$. *Tri-bromo-thioxene*. [141°]. Crystallises and sublimes in needles. Formed by the action of an excess of bromine upon the di-bromo- derivative of the thioxene obtained from acetonyl-acetone (Paal, *B.* 18, 2253).

Octo-bromo-di-methyl-thiophene $C_4Br_2(CBr_3)_2S$. *Octo-bromo-thioxene*. [114°]. Small needles. Formed by the action of an excess of bromine upon thioxene (from coal-tar) (Messinger, *B.* 18, 565).

BROMO-DI-METHYL-o-TOLUIDINE $C_9H_{12}BrN$ *i.e.* $C_6H_3(CH_3)(Br)NMe_2$. (245°). Prepared by bromination of di-methyl-*o*-toluidine, or by methylation of bromo-*o*-toluidine (Michler a. Sampaio, *B.* 14, 2172). Liquid; sol. alcohol and ether, volatile with steam.

Bromo-di-methyl-m-toluidine $C_6H_3(Br)(CH_3)NMe_2$ [1:2:4]. [98°]. (276°). Prepared by bromination of di-methyl-*m*-toluidine. White leaflets. Insol. water, sol. alcohol, ligroïn and C_6H_6 (Wurster a. Riedel, *B.* 12, 1800).

Ferrocyanide $B'_4H_4Fe(CN)_6 4aq$: crystals.

Ferricyanide $B'_4H_4Fe_2(CN)_{12}$ 9aq. Very soluble yellow crystals (Wurster a. Roser, *B.* 12, 1826).

TETRA-BROMO-MYRISTIC ACID $C_{14}H_{24}Br_4O_2$. From myristolic acid and Br (Masino, *A.* 202, 176).

DI-BROMO-MYRISTOLIC ACID $C_{14}H_{22}Br_2O_2$. Obtained by gently warming the preceding (M.).

α-BROMO-NAPHTHALENE $C_{10}H_7Br$ [1]. [5°]. (277°); (280° cor.) (Ramsay a. Young, *C. J.* 47, 650). S.G. $\frac{28}{4}$ 1·4750; ^{12} 1·503. R_∞ 84·9 (Nasini, *G.* 15, 93).

Formation.—1. From naphthalene in CS_2 and Br (Laurent, *A. Ch.* [2] 59, 196; Glaser, *A.* 135, 40; Wahlforss, *Z.* 1865, 3; Gnehm, *B.* 15, 2721).—2. From diazo-bromo-naphthalene salts by boiling with alcohol (Rother, *B.* 4, 851; Stallard, *C. J.* 49, 188).—3. From $Hg(C_{10}H_7)_2$ and Br (Otto, *A.* 147, 175).

Properties.—Liquid, insol. water, miscible with alcohol, ether, and benzene.

Reactions.—1. CrO_3 gives phthalic acid (Beilstein a. Kurbatow, *C. C.* 1881, 359).—2. A solution in CS_2 gently heated with Al_2Cl_6 gives (β)-bromo-naphthalene as the chief product, together with di-bromo-naphthalenes, and naphthalene (Roux, *Bl.* [2] 45, 510).—3. Toluene in presence of Al_2Cl_6 forms bromo-toluene and naphthalene (Roux).—4. Reduced by *sodium-amalgam* to naphthalene.—5. $Cl.CO_2Et$ and Na give naphthoic acid.

Picric acid compound $C_{10}H_7BrC_6H_2(NO_2)_3OH$. [135°]. Yellow needles (Wichelhaus, *B.* 2, 305; R.).

Dichloride $C_{10}H_7BrCl_2$: [165°]; tables.

(β)-Bromo-naphthalene $C_{10}H_7Br$ [2]. [59°]. (282 cor.). S. (92 p.c. alcohol) 6 at 20°.

Formation.—1. By heating (β)-diazo-naphthalene with a large excess of HBr (Gasiorowski a. Wayss, *B.* 18, 1911; *cf.* Liebermann, *A.* 183, 268). 2. By running a solution of (β)-diazo-naphthalene bromide into a hot solution of cuprous bromide; the yield is 30 p.c. of theoretical (Lellmann a. Remy, *B.* 19, 811).—3. From (β)-naphthol and PBr_5 (Brunel, *B.* 17, 1179).—4. From (α)-bromo-naphthalene and Al_2Cl_6 (Roux, *Bl.* [2] 45, 513).

Properties.—Trimetric scales, v. sol. CS_2, $CHCl_3$, benzene, and ether.

Picric acid compound $C_{10}H_7BrC_6H_2(NO_2)_3OH$. [79°] (R.); [86°] (B.); S. (alcohol of 92 p.c.) 6 at 20° (R.).

Di-bromo-naphthalene $C_{10}H_6Br_2$. [61°]. Formed in small quantity by brominating naphthalene (Jolin, *Bl.* [2] 28, 514; not observed by others).

o-Di-bromo-naphthalene $C_{10}H_6Br_2$ [1:2]. [63°]. From (1, 2)-bromo-(β)-naphthylamine by the diazo-perbromide reaction (Meldola, *C. J.* 43, 5). Oblique rhombic prisms (from alcohol, acetone or petroleum).

m-Di-bromo-naphthalene $C_{10}H_6Br_2$ [1:3]. [64°]. From di-bromo-(α)-naphthylamine, [119°] by removal of NH_2 (Meldola, *C. J.* 43, 2). Needles.

Di-bromo-naphthalene $C_{10}H_6Br_2$ [2:3]? [c. 68°]. Formed, together with two isomerides, [81°] and [150°] by the action of Br (2 mols.) on naphthalene (1 mol.) (Guareschi, *G.* 7, 24). Also from bromo-(β)-naphthol and PBr_5 (Canzoneri, *G.* 12, 425). Prisms (from alcohol).

(αβ')-Di-bromo-naphthalene $C_{10}H_6Br_2$ [4:2' or 3']. [74°]. From (4, 2' or 3', 2)-di-bromo-naphthylamine by diazo- reaction (Meldola, *C. J.* 47, 513). Silvery scales (from dilute alcohol).

η-Di-bromo-naphthalene $C_{10}H_6Br_2$ [1:x]. [77°]. Formed, together with the isomeride [1?°], by brominating naphthalene (α)-sulphonic acid (Darmstädter a. Wichelhaus, *A.* 152, 304).

(β)-Di-bromo-naphthalene $C_{10}H_6Br_2$ [1:4]. [82°]. (310°). S. (93·5 per cent. alcohol) 1·33 at 11·4°; 6 at 56° (Guareschi, *A.* 222, 269).

Formation.—1. The chief product of the action of bromine (2 mols.) on naphthalene (Glaser, *A.* 135, 40).—2. By distilling (α)-bromo-naphthalene sulphonic acid or nitro-(α)-bromo-naphthalene [85°] with PBr_5 (Jolin, *Bl.* [2] 28, 514).—3. From acetyl-(α)-naphthylamine by brominating, saponifying, and treating the resulting $C_{10}H_6Br(NH_2)$ by the diazo- reaction (Meldola, *C. J.* 43, 4).

Properties.—Long needles. Oxidised by HNO_3 to di-bromo-phthalic and bromo-nitro-phthalic acids and bromo-nitro-naphthalene. CrO_3 in acetic acid gives di-bromo-naphthoquinone and di-bromo-phthalide. Reacts with

Br forming $C_{10}H_4Br_8$ [173°] (Guareschi, *G.* 16, 141).

Constitution.—This follows from the oxidation to di-bromo-phthalic acid, coupled with the observation that the bromo-(α)-naphthylamine from which it may be formed (*v. supra*) gives (α)-bromo-naphthalene by the diazo- reaction.

(γ) **Di-bromo-naphthalene** $C_{10}H_6Br_2$ [1:1′or4′]. [131° cor.]. (326°). S. (93·5 p.c. alcohol) 2 at 56°.

Formation.—1. By brominating naphthalene (G.; Magatti, *G.* 11, 357).—2. From diazo-bromo-naphthalene (from bromo-naphthylamine [64°]) by adding bromine-water and warming the pp. with HOAc.—3. The chief product of the action of Br on naphthalene (α)-sulphonic acid (Darmstädter a. Wichelhaus, *A.* 152, 303).—4. By the action of PBr_5 on (α)-di-nitro-naphthalene or bromo-naphthalene (α)-sulphonic acid (J.).

Properties.—Tables. HNO_3 gives bromo-nitro-phthalic acid. CrO_3 in HOAc gives bromo-phthalic acid [176°]. Does not form a tetra-bromide with Br.

δ-Di-bromo-naphthalene $C_{10}H_6Br_2$. [141°]. From naphthalene (α)-sulphonic acid and PBr_5 (J.). Thin plates.

ϵ-Di-bromo-naphthalene $C_{10}H_6Br_2$. [160°]. From (α)-bromo-naphthalene sulphonic acid and PBr_5 (J.).

Di-bromo-naphthalene tetra-chloride $C_{10}H_6Br_2Cl_4$. [156°]. From di-brominated naphthalene (? [82°]) and Cl (Laurent).

Di-bromo-naphthalene tetra-bromide $C_{10}H_6Br_6$. A mixture of three bodies of this composition, [c. 100°] [120°] and [173°] is formed from naphthalene and Br (G.).

Tri-bromo-naphthalene $C_{10}H_5Br_3$. [75°]. Formed by brominating naphthalene, or by heating di-bromo-naphthalene tetra-bromide with alcoholic KOH (Laurent, *A. Ch.* [2] 59, 196; Glaser, *A.* 135, 43). Needles (from alcohol).

Tri-bromo-naphthalene $C_{10}H_5Br_3$ [1:4:1′]. [85°]. From di-bromo-nitro-naphthalene [117°] and PBr_5 (Jolin). Needles.

Tri-bromo-naphthalene $C_{10}H_5Br_3$ [87°]. From di-bromo-naphthalene (β)-sulphonic acid and PBr_5 (J.). Needles.

Tri-bromo-naphthalene $C_{10}H_5Br_3$ [1:3:1′or4′]. [105°]. From (3, 1′ or 4′, 1)-di-bromo-naphthylamine [102°] by diazo- reaction (Meldola, *C. J.* 47, 516).

Tri-bromo-naphthalene $C_{10}H_5Br_3$ [1:3:2′or3′]. [110°]. From (1, 2′ or 3′, 3)-di-bromo-naphthylamine by the diazo- reaction. Needles (from alcohol) (Meldola, *C. J.* 47, 513).

Tri-bromo-naphthalene $C_{10}H_5Br_3$ [1:2:4]. [114°]. From $C_{10}H_5(NH_2)Br_2$ [1:2:4] by diazo-reaction (Meldola, *C. J.* 43, 4). Formed also by heating $C_{10}H_5(NH_2)(NO_2)Br$ [1:2:4] with conc. HBrAq and glacial HOAc at 130° (Prager, *B.* 18, 2163). White needles (from dilute $C_2H_4O_2$). Dilute HNO_3 at 180° gives phthalic acid.

Tetra-bromo-naphthalene $C_{10}H_4Br_4$ [1:4:2′:3′]. [175°]. S. (95 p.c. alcohol) ·5 at 78°. From di-bromo-naphthalene tetrabromide [173°] and NaOEt (Guareschi, *G.* 16, 141). Needles (from alcohol) or plates (by sublimation). CrO_3 in HOAc gives di-bromo-phthalide [188°] and tetra-bromo-(α)-naphthoquinone [224°].

Tetra-bromo-naphthalene $C_{10}H_4Br_4$. [120°]. From di-bromo-naphthalene tetrabromide [100°] and NaOEt (Gu.). Needles (from alcohol).

Tetra-bromo-naphthalene tetra-bromide $C_{10}H_4Br_8$. [173°]. From (1,4)-di-bromo-naphthalene and Br (Gu.).

Penta-bromo-naphthalene $C_{10}H_3Br_5$. From $C_{10}H_4Br_4$ and Br at 150° (Glaser). Granules, insol. alcohol.

Hexa-bromo-naphthalene $C_{10}H_2Br_6$. [252°]. From naphthalene, Br, and I at 400° (Gessner, *B.* 9, 1505). Also from naphthalene (20 g.), Al_2Cl_6 (15 g.) and Br (300 g.) (Roux, *Bl.* [2] 45, 515). Needles; easily sublimed. Does not combine with picric acid.

BROMO-NAPHTHALENE DI-CARBOXYLIC ACID $C_{12}H_7BrO_4$ *i.e.* $C_{10}H_5Br(CO_2H)_2$. [210°]. From bromo-acenaphthene and CrO_3 (Blumenthal, *B.* 7, 1095). Needles (from benzene). Converted by NH_3 into the imide $C_{10}H_5Br(CO)_2NH$ [above 265°].

BROMO-NAPHTHALENE-(β)-SULPHINIC ACID $C_{10}H_6BrSO_2H$. From naphthalene (β)-sulphinic acid and Br (Gessner, *B.* 9, 1503).

(α)-BROMO-NAPHTHALENE SULPHONIC ACID $C_{10}H_6Br(SO_3H)$[1:4]. [139°]. Formed by sulphonating (α)-bromo-naphthalene (Laurent, *Compt. chim.* 1849, 392; Darmstädter a. Wichelhaus, *A.* 152, 303; Otto, *A.* 147, 184). Flat needles. Oxidised by $KMnO_4$ to phthalic acid (Meldola, *B.* 12, 1964). Potash-fusion gives no bromo-naphthol (M.). Br gives chiefly $C_{10}H_6Br_2$ [82°].—CaA'_2 3aq.—BaA'_2 2aq.—PbA'_2 1½aq.

Chloride $C_{10}H_6Br(SO_2Cl)$. [87°]. (Jolin, *Bl.* 28, 516). In its preparation there is also formed $C_{10}H_6Cl(SO_2Br)$ [116°] (Gessner, *B.* 9, 1504).

Bromide $C_{10}H_6Br(SO_2Br)$ [115°] (J.).

Amide $C_{10}H_6Br(SO_2NH_2)$ [190°] (J.); [195°] (O.).

Bromo-naphthalene (α)-sulphonic acid $C_{10}H_6Br(SO_3H)$. [104°]. Formed by brominating naphthalene (α)-sulphonic acid (D. a. W.). PBr_5 gives di-bromo naphthalene [131°].—KA′.

Chloride $C_{10}H_6Br(SO_2Cl)$ [90°] (J.).

Amide $C_{10}H_6Br(SO_2NH_2)$ [205°] (J.).

Bromo-naphthalene (β)-sulphonic acid $C_{10}H_6Br(SO_3H)$. [62°]. Formed by brominating naphthalene (β)-sulphonic acid (D. a. W.). Crystalline mass, sol. ether (difference from the two preceding acids).—KA′.

Bromo-naphthalene sulphonic acid $C_{10}H_6Br(SO_3H)$. Formed in small quantity in preparing its isomeride [139°] by sulphonating (α)-bromo-naphthalene with H_2SO_4 or $ClSO_3H$ (Armstrong a. Williamson, *C. J. Proc.* 1, 234).

Chloride $C_{10}H_6BrSO_2Cl$ [151°].

Di-bromo-naphthalene (β)-sulphonic acid $C_{10}H_5Br_2(SO_3H)$. Formed by brominating naphthalene (β)-sulphonic acid (J.). Crystalline. PBr_5 gives tri-bromo-naphthalene [87°].

Chloride $C_{10}H_5Br_2(SO_2Cl)$ [109°].

Amide $C_{10}H_5Br_2(SO_2NH_2)$ [238°].

Di-bromo-naphthalene sulphonic acid $C_{10}H_5Br_2(SO_3H)$. Got by sulphonating di-bromo-naphthalene (Laurent, *A.* 72, 299).—KA′.—BaA'_2.

BROMO-NAPHTHALIC ACID *v.* BROMO-OXY-(α)-NAPHTHOQUINONE.

BROMO-(α)-NAPHTHOIC ACID $C_{11}H_7BrO_2$ *i.e.* $C_{10}H_6Br.CO_2H$ [1:4′]. [246°] (Ek-

strand, *B.* 19, 1135). Produced from its nitrile or by brominating (α)-naphthoic acid (Hausamann, *B.* 9, 1516). White needles (by sublimation).—$KA'\frac{1}{2}aq$.—$CaA'_2 1\frac{1}{2}aq$. S. 1·5 at 20°.—$BaA'_2 3aq$. S. 1·7 at 21°.—AgA'.

Amide $C_{10}H_6Br.CONH_2$: [211°]; flat needles.

Nitrile $C_{10}H_6Br.CN$. [147°]. From (α)-naphthonitrile in CS_2 and Br.

Bromo-(β)-naphthoic acid $C_{10}H_6Br.CO_2H$. [256°]. From (β)-naphthoic acid and Br (H.). Needles (by sublimation).—$KA'2\frac{1}{2}aq$.—$CaA'_2 3aq$. S. ·02 at 20°.—$BaA'_2 3aq$. S. ·023 at 21°.—AgA'.

Nitrile $C_{10}H_6Br.CN$: [149°]; flat needles.

Tri-bromo-(β)-naphthoic acid $C_{10}H_4Br_3.CO_2H$. [270°]. From (β)-naphthoic acid (1 mol.), Br (3 mols.), and I at 350°. Needles (by sublimation).—BaA'_2 (H.).

Tetra-bromo-(α)-naphthoic acid $C_{10}H_3Br_4.CO_2H$. [239°]. From (α)-naphthoic acid (1 mol.) and Br (4½ mols.) at 350° (H.). Granules (from alcohol) or needles (by sublimation).—BaA'_2.

Tetra-bromo-(β)-naphthoic acid $C_{10}H_3Br_4.CO_2H$. [260°]. Preparation and properties similar to those of the preceding acid (H.).

BROMO-(α)-NAPHTHOL. *Ethyl ether* $C_{10}H_6Br(OEt)$. [48°]. From ethyl bromo-(α)-naphthol and Br (Marchetti, *C. N.* 40, 87). Prisms, v. sol. ether.

Bromo-(β)-naphthol $C_{10}H_6Br(OH)$ [3:2]?. [84°]. Prepared by adding Br in glacial acetic acid slowly to naphthol in glacial acetic acid (A. J. Smith, *C. J.* 35, 789). Needles. Sol. alcohol, ether, light petroleum and benzene. At 130° it begins to decompose, giving off HBr. Oxidised by alkaline $KMnO_4$ to phthalic acid. PBr_5 gives di-bromo-naphthalene [68°] and (β)-bromo-naphthalene (Canzoneri, *G.* 12, 424).

Acetyl derivative $C_{10}H_6Br(OAc)$. (215°) at 20 mm. (C.).

Nitroso- derivative $C_{10}H_5(NO)Br(OH)$. [65°]: green needles.

Di-bromo-(α)-naphthol $C_{10}H_5Br_2(OH)$ [1:3:4]. [106°] (Fittig, *A.* 227, 241). Formed by brominating (α)-naphthol in HOAc (Biedermann, *B.* 6, 1119) and in small quantity from di-bromo-(α)-naphthylamine by the diazo- reaction (Meldola, *C. J.* 45, 161). Long needles (from alcohol). Powerful oxidising agent.

Reactions.—1. $KMnO_4$ gives phthalic acid.—2. Alcoholic KOH gives tri-oxy-naphthalene.—3. Combines with *aniline* forming a white crystalline salt. If this is heated for 10 minutes at 200°, and then allowed to cool, crystals of $C_{10}H_5(NPhH)\Big<{OPh \atop N}$ or (β)-naphthoquinone di-anilide (*q.v.*) are got (Meldola, *C. J.* 45, 156).—4. *p-Toluidine* forms the corresponding (β)-naphthoquinone di-toluide (*q.v.*).—5. (β)-*naphthylamine* forms the corresponding (β)-naphthoquinone di-naphthalide (*q. v.*).

Tetra-bromo-(β)-naphthol $C_{10}H_3Br_4OH$. [156°]. Prepared by adding excess of bromine to (β)-naphthol dissolved in glacial acetic acid (A. J. Smith, *C. J.* 35, 791). White needles (from glacial acetic acid). Sol. CS_2, benzene and alkalis. Oxidised by $KMnO_4$ and KOH to bromo-phthalic acid (anhydride [125°]). Hence it is $C_6HBr_3(C_4H_2BrOH)$.

Penta-bromo-(α)-naphthol $C_{10}H_2Br_5.OH$ [2:4:1':3':4':1]. [239°]. Formed by bromination of (α)-naphthol in presence of Al_2Br_6. Slender felted needles. Sl. sol. benzene, xylene, and cumene, nearly insol. alcohol and ether. Dissolves in alkalis. By dilute HNO_3 at 100° it is oxidised to tetra-bromo-(α)-naphthoquinone [265°]; at 150° it is oxidised to di-bromo-phthalic acid [206°].—$C_{10}H_2Br_5.ONa$: long easily soluble needles.—$C_{10}H_2Br_5.OK$: small colourless needles (Blümlein, *B.* 17, 2485).

Penta-bromo-(β)-naphthol $C_{10}H_2Br_5(OH)$. [237°]. Formed by bromination of (β)-naphthol in presence of Al_2Br_6. White needles. Insol. alcohol, sl. sol. benzene. It is oxidised by HNO_3 to tetra-bromo-(β)-naphthoquinone; on further oxidation it yields tri-bromo phthalic acid $C_{10}H_2Br_5(ONa)$: long white silky needles (Flessa, *B.* 17, 1479).

Bromo-(β)-naphthol (α)-sulphonic acid $C_{10}H_5Br(OH)SO_3H$. [3:2:1]?

Salts.—Formed by adding the calculated quantity of bromine to saturated solutions of the salts of (β)-naphthol (α)-sulphonic acid (Armstrong a. Graham, *C. J.* 39, 137).—KA'. S. ·4 at 15°. Boiling HNO_3 forms phthalic acid.—$CaA'_2 xaq$.

BROMO-(α)-NAPHTHOQUINONE

Anilide $C_{10}H_4Br(NHC_6H_5)O_2$. [166°]. Formed by the action of aniline on bromo-oxy-(α)-naphthoquinone [197°] in acetic acid solution. Red prisms. Sol. hot alcohol and hot acetic acid. By cold aqueous NaOH it is split up into its constituents (Baltzer, *B.* 14, 1902).

An isomeric *anilide* $C_{10}H_4Br(NPhH)O_2$ [2:3:4:1] [191°] is formed by boiling di-bromo-(α)-naphthoquinone [218°] with an alcoholic solution of aniline. It is converted by KOH into bromo-oxy-(α)-naphthoquinone [202°] (Miller, *Bl.* [2] 43, 125).

p-Bromo-anilide $C_{10}H_4Br(NHC_6H_4Br)O_2$. [240°]. Prepared by bromination of (α)-naphthoquinone-anilide, or by boiling a mixture of *p*-bromo-anilin and bromo-oxy-(α)-naphthoquinone with acetic acid. Red needles. Sol. benzene, sl. sol. alcohol. By alcoholic H_2SO_4 it is decomposed into bromo-oxy-(α)-naphthoquinone and *p*-bromo-aniline (Baltzer, *B.* 14, 1901).

Bromo-(β)-naphthoquinone $C_6H_4\Big<{CO.CO \atop CH:CBr}\Big>$. [178°]. Obtained by bromination of (β)-naphthoquinone in acetic acid. Red needles or prismatic crystals. M. sol. warm alcohol, benzene, and acetic acid. Sublimable. Dissolves in dilute caustic alkalis with a brownish red colour, forming bromo-oxy-(α)-naphthoquinone [196°] (Zincke, *B.* 19, 2495).

Di-bromo-(α)-naphthoquinone $C_{10}H_4Br_2O_2$. [151°]. S. (alcohol) ·98 at 13°. Formed by the action of Br (7 pts.) and I (2 pts.) on (α)-naphthol (1 pt.) in presence of water (Diehl a. Merz, *B.* 11, 1065). Yellow needles; may be sublimed. Alkalis form HBr and bromo-oxy-naphthoquinone.

Di-bromo-naphthoquinone $C_{10}H_4Br_2O_2$. [171°-173°] [1:4:1':4']? S. (95 p.c. alcohol) ·31 at 16°. From di-bromo-naphthalene [82°], CrO_3 and glacial acetic acid (Guareschi, *A.* 222, 279). Yellow needles (from alcohol). Insol. water. Cannot be sublimed. Volatile with steam. CrO_3 does not oxidise it to di-bromo-phthalide.

Di-bromo-(β)-naphthoquinone $C_{10}H_4Br_2O_2$ [1:2:3:4]. [174°]. Obtained by the action of bromine upon bromo-(β)-naphthoquinone in hot acetic acid, or better upon (α)-amido-(β)-naphthol or its sulphate. Thick red plates or tables. Sl. sol. alcohol and ether (Zincke, *B.* 19, 2196).

Di-bromo-naphthoquinone $C_{10}H_4Br_2O_2$. [218°]. From (α)-naphthoquinone, Br, and I (Miller, *Bl.* [2] 38, 138). Prisms. Converted by KOH into bromo-oxy-naphthoquinone [200°].

Anilide [194°].

Tetra-bromo-(α)-naphthoquinone $C_{10}H_2Br_4O_2$. [265°]. Yellow plates. Sl. sol. alcohol. Formed by oxidation of penta-bromo-(α)-naphthol with dilute HNO_3 at 100°. By further oxidation at 150° it yields di-bromo-phthalic acid [206°] (Blümlein, *B.* 17, 2488).

Tetra-bromo-[α]-naphthoquinone $C_{10}H_2Br_4O_2$ [1':4':2:3:1:4]. [224°]. Formed by oxidising tetra-bromo-naphthalene [173°]. Orange-yellow prisms, v. sol. hot water (Guareschi, *G.* 16, 149).

Tetra-bromo-(β)-naphthoquinone $C_{10}H_2Br_4O_2$. [164°]. Red granular crystals. Sl. sol. alcohol. Formed by oxidation of penta-bromo-(β)-naphthol with dilute HNO_3. By further oxidation it is converted into tri-bromo-phthalic acid (Flessa, *B.* 17, 1481).

BROMO-NAPHTHOSTYRIL *v. Inner anhydride of* BROMO-AMIDO NAPHTHOIC ACID.

DI-BROMO-(αα)-DINAPHTHYL $C_{20}H_{12}Br_2$. [215°]. From di-naphthyl and bromine-vapour (Lossen, *A.* 144, 77). Monoclinic prisms; v. sl. sol. alcohol.

Hexa-bromo-(αα)-dinaphthyl $C_{20}H_8Br_6$. Resin.

Hepta-bromo-(ββ)-dinaphthyl $C_{20}H_7Br_7$. Amorphous (Smith a. Poynting, *C. J.* 27, 851).

BROMO-NAPHTHYLAMINE $C_{10}H_6Br(NH_2)$. By reduction of bromo-nitro-naphthalene [85°] of Jolin, itself got from (α)-bromo-naphthalene by nitration. An oil. May be distilled with steam. Fe_2Cl_6 gives a violet colour in its aqueous solution. Reduces $AgNO_3$ (Guareschi, *A.* 222, 299). Possibly identical with Rother's (1, 4)-bromo-naphthylamine [94°].

m-**Bromo-(α)-naphthylamine** $C_{10}H_6Br(NH_2)$ [3:1]. [62°]. From the nitro- compound, zinc-dust, and HOAc (Meldola, *C. J.* 47, 509). Needles (from dilute alcohol).

Acetyl derivative $C_{10}H_6Br(NHAc)$ [187°]: needles.

o-**Bromo-(β)-naphthylamine** $C_{10}H_6(Br)NH_2$ [1:2]. [63°]. Got by saponification of the acetyl derivative obtained by bromination of acetyl (β)-naphthylamine [131°]. Small white needles. Volatile with steam. It is a neutral body. Dilute HNO_3 gives phthalic acid (Meldola, *C. J.* 43, 6). When NH_2 is displaced by H (α)-bromo-naphthalene results (M.).

Acetyl derivative $C_{10}H_6Br.NH(Ac)$ [135°]. Needles (Cosiner, *B.* 14, 59).

Bromo-(α)-naphthylamine $C_{10}H_6Br(NH_2)$ [1:1' or 4']. [64°]. From bromo-nitro-naphthalene [122·5°] (Guareschi, *A.* 222, 297). Volatile with steam. Plates (from boiling water). May be sublimed. $KMnO_4$ forms *c*-bromo-phthalic acid [165°-172°].—B'HCl.

m-**Bromo-(β)-naphthylamine** $C_{10}H_6Br(NH_2)$ [1:3]. [72°]. From Liebermann's bromo-nitro-naphthalene by reduction (Meldola, *C. J.* 47, 509). Converted into (1, 3)-di-bromo-naphthalene by the diazo- reaction.

Acetyl derivative $C_{10}H_6Br(NHAc)$. [187°]: needles.

p-**Bromo-(α)-naphthylamine** $C_{10}H_6Br(NH_2)$ [1:4]. [94°]. From its acetyl derivative and KOH (Rother, *B.* 4, 850; Meldola, *B.* 12, 1961). Needles. On oxidation it gives phthalic acid. By diazo- reaction it gives (α)-bromo-naphthalene. Br gives di-bromo-naphthylamine [119°].

Acetyl derivative $C_{10}H_6Br.NHAc$. [192°]. Prepared by slowly adding HCl to a solution of bromine in NaOH in which is suspended acetyl-(α)-naphthylamine. White needles (Prager, *B.* 18, 2159).

Di-bromo-(α)-naphthylamine $C_{10}H_5Br_2(NH_2)$ [3:2'or3':1]? [102°]. From its acetyl derivative. Needles; sol. boiling dilute acids. Removal of NH_2 gives di-bromo-naphthalene [74°] (? [1:1']).

Acetyl derivative $C_{10}H_5Br_2(NHAc)$ [221°]. From acetyl-(3, 1)-bromo-naphthylamine and Br (Meldola, *C. J.* 47, 514).

Di-bromo-(α)-naphthylamine $C_{10}H_5Br_2(NH_2)$ [1':3:1]. [105°]. From its acetyl derivative. Needles. Oxidised by dilute HNO_3 to *c*-bromo-phthalic acid [174°]. Converted into di-bromo-naphthalene [74°] by diazo- reaction.

Acetyl derivative $C_{10}H_5Br_2(NHAc)$. [222°]. From bromo-naphthylamine [62°] by acetylation and bromination (Meldola, *C. J.* 47, 512; *C. J. Proc.* 1, 173).

Di-bromo-(α)-naphthylamine $C_{10}H_5Br_2(NH_2)$ [1:3:4]. [119°]. From the acetyl derivative by hot aqueous KOH. Needles; does not combine with acids. Oxidation gives phthalic acid; the diazo- reaction gives (1, 3)-di-bromo-naphthalene.

Acetyl derivative $C_{10}H_5Br_2(NHAc)$. [225°]. Formed by bromination of acetyl-(α)-naphthylamine (Meldola, *B.* 12, 1961).

Di-bromo-(β)-naphthylamine $C_{10}H_5Br_2(NH_2)$ [121°]. Long colourless needles. Formed by the action of bromine in acetic acid solution upon (β)-naphthalene-azo-(β)-naphthylamine.

Acetyl derivative: [208°] (Lawson, *B.* 18, 2424).

Tetra-bromo-naphthylamine

Acetyl derivative $C_{10}H_3Br_4NHAc$. [138°]. Formed by brominating acetyl-(1,2)-bromo-(β)-naphthylamine in acetic acid solution (Meldola, *C. J.* 43, 8). Minute needles (from alcohol). Could not be saponified.

BROMO-NAPHTHALENE-DIAMINE.

Acetyl derivative $C_{10}H_5Br(NH_2)(NHAc)$ [2:4:1] [c. 222°]. From bromo-nitro-acetnaphthalide. Is not basic (Meldola, *C. J.* 47, 499).

Di-bromo-(1:1'or4')-naphthylene-diamine $C_{10}H_4Br(NH_2)_2$. From naphthylene-diamine hydrochloride (from (α)-di-nitro-naphthalene) and bromine-water (Hollemann, *Z.* 1865, 556).

DI-BROMO-(α)-DINAPHTHYLENE-OXIDE $C_{20}H_{10}Br_2O$. [287°]. Light-yellow crystals. Sl. sol. benzene and acetic acid. Prepared by the action of Br on a CS_2 solution of (α)-dinaphthylene-oxide (Knecht a. Unzeitig, *B.* 13, 1725).

Di-bromo-(β)-dinaphthylene-oxide $C_{20}H_{10}Br_2O$. [247°]. Yellow needles. Prepared by the action of bromine on a CS_2 solution of (β)-dinaphthylene-oxide (K. a. U.).

DI-BROMO-DI-NAPHTHYL-METHANE $C_{21}H_{14}Br_2$. [193°]. From di-naphthyl-methane and Br (Grabowski, *B.* 7, 1605). Needles (from

alcohol-benzene); not affected by boiling alcoholic KOH.

BROMO-NICOTINE *v.* NICOTINE.

BROMO-o-NITRO-ACETOPHENONE $C_8H_6BrNO_3$ *i.e.* [2:1] $C_6H_4(NO_2).CO.CH_2Br$. [56°]. By bromination of $C_6H_4(NO_2).CO.Me$ (Gevekoht, *A.* 221, 327). Needles (from benzoline).

Bromo-m-nitro-acetophenone [3:1] $C_6H_4(NO_2).CO.CH_2Br$. *Nitro-phenyl bromo-methyl ketone.* [96°]. Formed by nitrating bromo-acetophenone. Needles (from dilute alcohol); v. sl. sol. ether. Oxidation gives *m*-nitro-benzoic acid (Hunnius, *B.* 10, 2008).

Di-bromo-o-nitro-acetophenone $C_6H_4(NO_2).CO.CHBr_2$. [86°]. Prepared like the above (G.). Attacks the eyes. Prisms (from benzoline).

ω-Di-bromo-m-nitro-acetophenone $C_6H_4(NO_2).CO.CHBr_2$. *m-Nitro-phenyl di-bromo-methyl ketone.* [59°]. Formed by careful nitration of ω-di-bromo-acetophenone; or by further bromination of ω bromo-*m*-nitro-acetophenone. Yellowish tables. V. sol. most solvents (Engler a. Hassenkamp, *B.* 18, 2240).

BROMO-NITRO-o-AMIDO-BENZOIC ACID $C_6H_2Br(NO_2)(NH_2)CO_2H$ [1:2?:4:5]. [272°]. Formed by treating nitro-isatoic acid at 100° with bromine dissolved in glacial acetic acid (Dorsch, *J. pr.* [2] 33, 40). Long yellow needles. Sol. hot water, acetone, alcohol, glacial acetic acid and ether. Insol. chloroform and benzene.

Di-bromo-nitro-o-amido-benzoic acid $C_6HBr_2(NO_2)(NH_2)CO_2H$. [c. 203°]. From nitro-isatoic acid and bromine in glacial acetic acid at 100° (D.). Plates. Sol. acetone, alcohol and glacial acetic acid, less sol. benzene, chloroform, and ether, insol. water.

Tri-bromo-nitro-o-amido-benzoic acid $C_6Br_3(NO_2)(NH_2)(CO_2H)$. [196°]. From nitro-isatoic acid and bromine (D.). Needles (ppd. by adding water to its solution in acetone). V. sol. acetone, alcohol, ether, glacial acetic acid, chloroform and benzene.

(3:5:4:1)-**BROMO-NITRO-AMIDO-PHENYL-ACETIC ACID** $C_6H_2(Br)(NO_2)(NH_2).CH_2.CO_2H$ [3:5:4:1]. [192°]. Prepared by saponification of the acetyl derivative of (3:5:4:1)-bromo-nitro-amido-benzyl cyanide (Gabriel, *B.* 15, 1994). Long yellow needles. Sol. hot alcohol, ether and acetic acid, sl. sol. cold water, benzene, and chloroform.

Nitrile $C_6H_2(Br)(NO_2)(NH_2).CH_2CN$ [3:5:4:1]. *Bromo-nitro-amido-benzyl cyanide. Acetyl derivative*: [191°]. Formed by nitration of the acetyl derivative of (3:4:1) bromo-amido-phenyl-aceto-nitrile (Gabriel, *B.* 15, 1992). Slender yellow needles, sol. alcohol and acetic acid, sl. sol. cold water, v. sl. sol. ether and CS_2.

BROMO-NITRO-ANILINE $C_6H_3Br(NO_2)(NH_2)$ [1:3:6]. [104°]. Formed by heating $C_6H_3Br_2(NO_2)$ [59°] with alcoholic NH_3 at 190° (Körner, *G.* 4, 371). Yellow needles; gives *m*-bromo-nitro-benzene by diazo-reaction. Br forms di-bromo-*p*-nitro-aniline [203°].

Benzoyl derivative $C_6H_3Br(NO_2)(NHBz)$. [160°]. From benzoyl-*p*-nitro-aniline and Br (Johnson, *B.* 10, 1709).

Bromo-nitro-aniline $C_6H_3Br(NO_2)(NH_2)$[1:3:4]. [111°]. S. ·014 at 20°; S. (alcohol) 10·4.

Formation.—1. From nitro-*p*-di-bromo-benzene and alcoholic NH_3 at 165° (K.; Meyer a. Wurster, *A.* 171, 59).—2. By nitrating *p*-bromo aniline in glacial HOAc (Hübner, *A.* 209, 357). 3. By the action of alcoholic NH_3 on the methyl derivative of (1,3,4)-bromo-nitro-phenol.

Properties.—Orange needles; may be sublimed; scarcely basic. Converted by diazo-reaction into *m*-bromo-nitro-benzene [56°].

Acetyl derivative $C_6H_3Br(NO_2)(NHAc)$. [103°]. Formed by nitrating acetyl-*p*-bromo-aniline (H.). Ammonia and zinc-dust reduce it to $C_6H_3Br(NHAc).N_2.C_6H_3Br(NHAc)$ [282°] (Matthiessen a. Mixter, *Am.* 8, 347).

Benzoyl derivative $C_6H_3Br(NO_2)(NHBz)$. [138°]. Formed by nitrating benzoyl-*p*-bromo-aniline or brominating benzoyl-*o*-nitro-aniline (Meinecke, *B.* 8, 564; Johnson, *B.* 10, 1710).

Bromo-nitro-aniline $C_6H_3Br(NO_2)(NH_2)$ [1:2:4]. [132°]. Formed by nitration of *p*-bromaniline dissolved in 10 pts. of H_2SO_4. Flat plates. V. sol. alcohol, ether, acetic acid, and chloroform, v. sol. water. By further bromination it yields tri-bromo-nitraniline [103°] (Nölting a. Collin, *B.* 17, 266).

Bromo-nitro-aniline $C_6H_3Br(NO_2)(NH_2)$ [1:4:5]. [151°]. Formed by the action of alcoholic NH_3 upon (1,5,4)-di-bromo-nitro-benzene [62°] or on (1,4,5)-bromo-di-nitro-benzene [56°] (K.; Wurster, *B.* 6, 1542). Orange needles. Gives by diazo-reaction *p*-bromo-nitro-benzene. Is not basic. Dilute HNO_3 (S.G. 1·38) slowly forms bromo-di-nitro-phenol [81°].

Bromo-di-nitro-aniline $C_6H_2Br(NO_2)_2(NH_2)$ [1:3:5:6]. [151°] (L.); [144°] (K.). Formed by brominating di-nitro-aniline (K.), or by heating di-nitro-methyl-aniline with HOAc and Br (Leymann, *B.* 15, 1234). Yellow needles. Converted by boiling KOH into bromo-di-nitro-phenol [118°].

Bromo-di-nitro-aniline $C_6H_2Br(NO_2)_2(NH_2)$. [160°]. From di-bromo-di-nitro-benzene [100°] and alcoholic NH_3 at 100° (Austen, *B.* 9, 919). Orange scales.

Bromo-di-nitro-aniline $C_6H_2Br(NO_2)_2(NH_2)$. [178°]. From di-bromo-di-nitro-benzene [117°] and alcoholic NH_3 (K.).

Bromo-di-nitro-aniline. *Benzoyl derivative* $C_6H_2Br(NO_2)_2(NHBz)$ [1:3:5:4]. [221°]. Small needles; formed by nitrating benzoyl bromo-nitro-aniline $C_6H_3Br(NO_2)(NHBz)$ [1:3:4], or benzoyl di-bromo-aniline (Johnson, *B.* 10, 1710).

Bromo-di-nitro-aniline. *Benzoyl derivative* $C_6H_2Br(NO_2)_2(NHBz)$. [196°]. Formed by nitrating benzoyl-*p*-bromo-aniline (Meinecke, *B.* 8, 561), is probably identical with the preceding.

Di-bromo-nitro-aniline $C_6H_2Br_2(NO_2)(NH_2)$. [75°]. From di-bromo-di-nitro-benzene [159°] and alcoholic NH_3 at 100° (Austen, *B.* 9, 622). Red needles.

Di-bromo-o nitro-aniline $C_6H_2Br_2(NO_2)(NH_2)$ [1:3:5:6]. [127°] (Hentschel, *J. pr.* [2] 34, 426).

Formation.—1. By brominating *o*-nitro-aniline or (1,3,4)-bromo-nitro-aniline.—2. By the action of alcoholic NH_3 on (1,3,4,5)-tri-bromo-nitro-benzene or the methyl ether of (1,3,5,6)-di-bromo-nitro-phenol (K.).

Properties.—Orange needles.

Acetyl derivative $C_6H_2Br_2(NO_2)(NHAc)$.

[209°]. From acetyl-di-bromo-aniline by nitration. Needles, v. sol. alkalis (Remmers, *B.* 7, 348).

Benzoyl derivative $C_6H_2Br_2(NO_2)(NHBz)$ [1:3:5:6]? [195°]. Formed by brominating benzoyl-*o*-nitro-aniline (Johnson, *B.* 10, 1710). Yellow needles.

Di-bromo-*p*-nitro-aniline $C_6H_2Br_2(NO_2)(NH_2)$ [1:3:5:2]. [207°] (L.); [203°] (K.).

Formation.—1. By brominating *p*-nitro-aniline or (1,3,6)-bromo-nitro-aniline.—2. By the action of alcoholic NH_3 on tri-bromo-nitro-benzene [112°] or the methyl ether of (1,3,5,2)-di-bromo-nitro-phenol (K.).—3. From tri-bromo-aniline in HOAc by warming with conc. HNO_3 for a short time (Losanitsch, *B.* 15, 474).

Properties.—Thin yellow needles. Displacement of NH_2 by H gives tri-bromo-benzene [112°].

Tri-bromo-nitro-aniline $C_6HBr_3(NO_2)(NH_2)$ [1:3:5:4:6]. [103°]. From *m*-nitro-aniline and bromine-vapour (K.), or from (1,2,4)-bromo-nitro-aniline and Br in HOAc (Nölting a. Collin, *B.* 17, 266). Pale greenish-yellow needles in stellate groups; v. sol. alcohol. Converted by diazo- reaction into (1,3,5,4)-tri-bromo-nitro-benzene.

Tri-bromo-nitro-aniline $C_6HBr_3(NO_2)(NH_2)$ [1:3:5:4:6]? [215°]. From its acetyl derivative (Remmers, *B.* 7, 351). Flat yellow needles; sl. sol. alcohol. This body might be expected to be identical with the preceding.

Acetyl derivative $C_6HBr_3(NO_2)(NHAc)$. [232°]. From acetyl-(1,3,5,6)-tri-bromo-aniline (R.). Needles.

Di-acetyl derivative $C_6HBr_3(NO_2)(NAc_2)$. Formed by nitrating di-acetyl-tri-bromo-aniline.

Tri-bromo-nitro-aniline $C_6HBr_3(NO_2)(NH_2)$ [1:2:3:5:6]. [161°]. From (1,2,4)-bromo-nitro-aniline [151°] and bromine vapour (K.). Lemon-yellow needles (from alcohol). Converted by diazo- reaction into (1,2,3,5)-tri-bromo-nitro-benzene [112°].

BROMO-NITRO-ANTHRAQUINONE

$C_{14}H_6(NO_2)(Br)O_2$. [261° uncor.]. Prepared by nitration of tetra-bromo-anthracene. White needles. Sublimable. Sol. acetic acid, sl. sol. alcohol, ether, and chloroform. On reduction it gives amido-anthraquinone (Claus a. Hertel, *B.* 14, 980).

Bromo-di-nitro-anthraquinone

$C_{14}H_5Br(NO_2)_2O_2$. [213° uncor.]. Prepared by nitration of tri bromo-anthracene with a mixture of fuming HNO_3 and fuming H_2SO_4. Yellow needles. Sol. benzene, chloroform, and acetic acid, m. sol. alcohol and ether (Claus a. Diernfellner, *B.* 14, 1333).

Di-bromo-nitro-anthraquinone

$C_{14}H_5Br_2(NO_2)O_2$. [245° uncor.]. Prepared by nitration of tetra-bromo-anthracene. Sublimable. Fine yellow needles. V. sol. hot acetic acid, less in alcohol and ether. On reduction with sodium-amalgam it gives amido-anthraquinone.

Di-bromo-di-nitro-anthraquinone

$C_{14}H_4Br_2(NO_2)_2O_2$. [239° uncor.]. Prepared by nitration of tetra-bromo-anthracene with a mixture of fuming H_2SO_4 and fuming HNO_3. Needles. Sol. acetic acid, benzene and chloroform, sl. sol. alcohol and ether (C. a. D.).

Tetra-bromo-di-nitro-anthraquinone

$C_{14}H_2(NO_2)_2Br_4O_2$. [105°]. Prepared by nitration of dibromo-anthracene-tetrabromide. Sol. alcohol, ether, benzene, and acetic acid. Not sublimable. On reduction it gives (*a*)-diamido-anthraquinone (Claus a. Hertel, *B.* 14, 981).

***p*-BROMO-*o*-NITRO-BENZALDOXIM**

$C_7H_5N_2O_3Br$ *i.e.* [2:4:1] $C_6H_3(NO_2)(Br)(CH:NOH)$ [153°]. Prepared by heating *o*-nitro-*p*-diazo-benzaldoxim with HBr (Gabriel a. Meyer, *B.* 14, 827). Fine needles. Sol. alcohol, ether, acetic acid, and hot benzene.

***o*-BROMO-NITRO-BENZENE** $C_6H_4Br(NO_2)$ [1:2]. Mol. w. 202. [41°] (F. a. M.); [43°] (K.). (261° i.V.). Formed, together with a much larger quantity of the *p*-isomeride, by nitrating bromo-benzene (Hübner a. Alsberg, *A.* 156, 316; *Z.* [2] 6, 369; Walker a. Zincke, *B.* 5, 114; Fittig a. Mager, *B.* 7, 1179). Yellow needles, more sol. alcohol than the *p*-isomeride.

Reactions.—1. $SnCl_2$ reduces it to *o*-bromo-aniline.—2. Alcoholic NH_3 at 190° gives *o*-nitro-aniline (W. a. Z.).—3. HNO_3 gives bromo-di-nitro-benzene [72°].—4. KCN and alcohol at 190° gives $C_6H_4Br.CN$.—5. Heating with KOHAq gives *o*-bromo-phenol.

***m*-Bromo-nitro-benzene** $C_6H_4Br(NO_2)$ [1:3]. [56°]. (257° i.V.).

Formation.—1. From *m*-nitro-aniline by the diazo- reaction (Griess, *T.* 1864 [3] 712).—2. From (1, 3, 4)-bromo-nitro aniline (Wurster, *B.* 6, 1513; 7, 416).—3. From nitro-benzene (10 g.), Fe_2Cl_6 (1 g.), bromine (13 g.) in sealed tubes for 12 hours at 70° (Scheufelen, *A.* 231, 165). The yield is 80 p.c. of the theoretical.—4. By the action of a hot solution of cuprous bromide upon *m*-nitro-diazo-benzene sulphate (from *m*-nitraniline) (Sandmeyer, *B.* 18, 1495).

Properties.—Yellow trimetric plates. Not attacked by KOHAq or alcoholic NH_3.

***p*-Bromo-nitro-benzene** $C_6H_4Br(NO_2)$ [1:4]. [126°]. (256° i.V.).

Formation.—1. The chief product obtained by dissolving bromo-benzene in fuming HNO_3 (Couper, *A.* 104, 226).—2. From *p*-nitro-aniline by the diazo- reaction.—3. From bromo-nitro-aniline [151°].—4. From bromo-benzene *p*-sulphonic acid and HNO_3 (Spiegelberg, *A.* 197, 257). 5. Formed by the action of precipitated Cu_2O (1 mol.) upon *p*-bromo-diazo-benzene nitrite (1 mol.) obtained by adding slowly a solution of 15 g. of $NaNO_2$ in 50 c.c. of water to a mixture of 17 g. of *p*-bromo-aniline, 20 g. HNO_3 (1·4), and 50 c.c. of water. The yield is small (Sandmeyer, *B.* 20, 1496).

Properties.—Long white needles, sl. sol. HOEt.

Reactions.—1. Resembles *o*-nitro-aniline in *reactions* 1 and 2.—2. Alcoholic KCN at 190° gives *m*-bromo-benzonitrile (Richter, *B.* 4, 462). 3. Br at 250° gives *p*-di-, *u*-tri-, and *s*-tetra-bromo-benzenes (Ador a. Rilliet, *J.* 1876, 370).

Bromo-di-nitro-benzene $C_6H_3Br(NO_2)_2$ [1:3:4]. [59°]. From *m*-bromo-nitro-benzene, HNO_3 and H_2SO_4 (Körner, *J.* 1875, 332) Monoclinic plates (from ether-alcohol). Alcoholic NH_3 at 180° forms $C_6H_3Br(NO_2)(NH_2)$ [1:4:3] [151°]. Boiling NaOHAq (S.G. 1·135) gives $C_6H_3Br(NO_2)(OH)$ [1:4:3] and a little $C_6H_3Br(NO_2)(OH)$ [1:3:4] (Laubenheimer, *B.* 11, 1159).

Bromo-di-nitro-benzene $C_6H_3Br(NO_2)_2$ [1:2:4]. [72°]. From bromo-benzene, fuming HNO_3, and H_2SO_4 in the cold (Kekulé, *A.* 137, 167; Spiegelberg, *A.* 197, 257). Large yellow prisms. Alcoholic NH_3 forms di-nitro-aniline. KOHAq forms di-nitro-phenol [114°]. Sn and HCl gives *m*-

phenylene-diamine (Zincke a. Sintenis, *B.* 5, 791). Crystallises with benzene as $(C_6H_3Br(NO_2)_2)_2C_6H_6$ [65°].

Bromo-di-nitro-benzene $C_6H_3Br(NO_2)_2$. [87°]. Di-bromo-di-nitro-benzene [158°] is treated with alcoholic NH_3 at 100° and in the resulting $C_6H_2Br(NO_2)_2(NH_2)$ hydrogen is substituted for NH_2 by the diazo- reaction (Austen, *B.* 8, 1183). Not affected by alcoholic NH_3.

Di-bromo-nitro-benzene $C_6H_3Br_2(NO_2)$ [1:2:4]. Mol. w. 281. [59°]. From o-di-bromo-benzene and HNO_3 (Riese, *A.* 164, 179). Monoclinic tables (Groth a. Bodewig, *B.* 7, 1563). May be reduced to di-bromo-aniline [80°].

Di-bromo-nitro-benzene $C_6H_3Br_2(NO_2)$ [1:3:4]. [62°]. Formed by nitrating *m*-di-bromo-benzene (Meyer a. Stüber, *A.* 165, 176). Triclinic prisms (by sublimation, G. a. B.); volatile with steam. Converted by alcoholic NH_3 at 190° into (1,4,3)-bromo-nitro-aniline. Reduction gives (1,3,4)-di-bromo-aniline. Alcoholic KCN at 250° gives the nitrile of di-bromo-benzoic acid [209°] (R.).

Di-bromo-nitro-benzene $C_6H_3Br_2(NO_2)$ [1:3:2]. [83°]. Separates from the alcoholic mother-liquors from which the preceding has crystallised. Prisms or laminæ. Alcoholic NH_3 at 190° gives nitro-*m*-phenylene-diamine (Körner, *G.* 4, 360).

Di-bromo-nitro-benzene $C_6H_3Br_2(NO_2)$ [1:4:5]. [85°]. From *p*-di-nitro-benzene by nitration (Riche a. Bérard, *A.* 133, 51). From *m*-bromo-nitro-benzene (14 g.), Br_2 (11·2 g.), and Fe_2Cl_6 (4 g.) at 80° for 12 hours (Scheufelen, *A.* 231, 169). Yellowish-green tablets (from ether-alcohol). Alcoholic NH_3 at 210° gives (1,3,4)-bromo-nitro-aniline. Sn and HCl gives *p*-di-bromo-aniline [51°]. Alcoholic KCN gives the nitrile of di-bromo-benzoic acid [152°].

Di-bromo-nitro-benzene $C_6H_3Br_2(NO_2)$ [1:3:5]. [105°]. From (1,5,3,6) or (1,5,3,2) di-bromo-nitro-aniline by diazo- reaction (Körner). Prisms or tablets (from ether). May be reduced to di-bromo-aniline [57°].

Di-bromo-di-nitro-benzene $C_6H_2Br_2(NO_2)_2$. [117°]. Formed by nitrating *m*-di-bromo-benzene (Körner). Greenish-yellow needles, volatile with steam. Heating with KOHAq gives bromo-di-nitro-phenol [92°].

Di-bromo-di-nitro-benzene $C_6H_2Br_2(NO_2)_2$. [58°]. Formed by nitrating *o*-di-bromo-benzene (Austen, *B.* 8, 1182). Prisms (from HOAc). By displacement of Br by NH_2 and H successively it may be converted into bromo-di-nitro-benzene [87°].

Di-bromo-di-nitro-benzene $C_6H_2Br_2(NO_2)_2$. [120°]. Formed in small quantities in the preparation of the preceding body (A.).

Di-bromo-di-nitro-benzene $C_6H_2Br_2(NO_2)_2$. [159°]. Formed by nitrating *p*-di-bromo-benzene (Austen, *B.* 9, 621). Small needles. Alcoholic NH_3 forms di-bromo-nitro-aniline [75°].

Di-bromo-di-nitro-benzene $C_6H_2Br_2(NO_2)_2$ [1:4:2:6]. [100°]. Formed in preparing the preceding (A.). Alcoholic NH_3 converts it into bromo-di-nitro-aniline [160°].

Tri-bromo-nitro-benzene $C_6H_2Br_3(NO_2)$ [1:3:4:6]. Mol. w. 360. [94°]. Formed by nitrating *u*-tri-bromo-benzene (Mayer, *A.* 137, 226). Pale yellowish-green needles (from alcohol). Alcoholic NH_3 gives bromo-nitro-*p*-phenylene-diamine.

Tri-bromo-nitro-benzene $C_6H_2Br_3(NO_2)$ [1:2:3:5]. [112°]. From (1,5,3,6)-di-bromo-nitro-aniline [203°] by displacing NH_2 by Br, or from (1,2,3,5,4) tri-bromo-nitro-aniline by displacing NH_2 by H (Körner). Triclinic crystals; $a:b:c = 1·005:1:·4823$ (La Valle, *G.* 10, 1). Reduction gives tri-bromo-aniline. Alcoholic NH_3 gives di-bromo-nitro-aniline [203°].

Tri-bromo-nitro-benzene $C_6H_2Br_3(NO_2)$ [1:2:4:6]. [120°]. From (2,4,6,1) di-bromo-nitro-aniline by diazo reaction (Körner). Needles (from HOAc). Alcoholic NH_3 gives the parent di-bromo-nitro-aniline.

Tri-bromo-nitro-benzene $C_6H_2Br_3(NO_2)$ [1:3:5:2]. [125°]. (177°) at 11 mm. Prepared by nitration of *s*-tri-bromo-benzene with HNO_3 (1·5) (Wurster a. Beran, *B.* 12, 1821; *cf.* C. L. Jackson, *B.* 8, 1172). Formed also by diazo- reaction from (1,3,5,2,4)-tri-bromo-nitro-aniline (Körner, *G.* 4, 422). Monoclinic prisms; $a:b:c = ·6518:1:·8695$; η - 99°46′ (Panebianco, *G.* 9, 354). Tin and HCl reduce it to ordinary tri-bromo-aniline. Alcoholic NH_3 at 170° gives (1,4,3,5)-bromo-nitro-phenylene-diamine.

Tri-bromo-nitro-benzene $C_6H_2Br_3(NO_2)$ [1:3:4:2]. [above 187°]. Formed in small quantity in preparing the isomeride [94°]. Sublimes at 187°.

Tri-bromo-di-nitro-benzene $C_6HBr_3(NO_2)_2$ [1:2:4:3:5?]. [135°]. Formed by nitrating the preceding body (Mayer). Triclinic crystals; $a:b:c = ·455:1:·457$ (Panebianco, *G.* 9, 355). Alcoholic NH_3 gives bromo-di-nitro-phenylene-diamine.

Tri-bromo-di-nitro-benzene $C_6HBr_3(NO_2)_2$ [1:3:5:2:6]. [192°]. Glistening needles. Prepared by nitration of *s*-tri-bromo-benzene with HNO_3 and H_2SO_4 (Wurster a. Beran, *B.* 12, 1821).

Tetra-bromo-nitro-benzene $C_6HBr_4(NO_2)$ [1:3:4:5:6]. [96° after several fusions]. Slender needles, [60°] (from alcohol). From *u*-tetra bromo-benzene by nitration. Formed also by heating $C_6(NO_2)Br_4SO_3H$ with HCl (V. v. Richter, *B.* 8, 1427; Langfurth, *A.* 191, 202).

Penta-bromo-nitro-benzene $C_6Br_5(NO_2)$. [228°]. From *u*-tetra-bromo-benzene and fuming HNO_3 (R.). Monoclinic prisms (from benzene).

BROMO - NITRO - BENZENE SULPHONIC ACID $C_6H_3Br(NO_2)(SO_3H)$ [1:4:2]. [130°-135°]. From bromo-benzene *o*-sulphonic acid and conc. HNO_3 (Bahlmann, *A.* 186, 315). From *p*-bromo-nitro-benzene and fuming H_2SO_4 (Augustin a. Post, *B.* 8, 1559). Flat yellow columns, v. e. sol. water. Reduction gives amido-benzene *m*-sulphonic acid; exchange of NO_2 for Br gives *p*-di-bromo-benzene sulphonic acid. - AgA′.—$BaA'_2$5aq. S. (of BaA'_2) 5·3 at 16°.—CaA'_2 4aq. —CaA'_2 6½aq (A. a. P.). — KA′. — NaA′.—NH_4A'. PbA'_2 5aq. ZnA'_2 7aq.

Chloride $C_6H_3Br(NO_2)(SO_2Cl)$: [92°]; tables.

Amide $C_6H_3Br(NO_2)(SO_2NH_2)$. [205°].

Bromo-nitro-benzene sulphonic acid $C_6H_3Br(NO_2)(SO_3H)$ [1:6:2]? Formed in small quantity in preparing the above by nitrating bromo-benzene *o*-sulphonic acid (B.).—BaA'_2. S. ·156 at 8°. KA′.

Chloride $C_6H_3Br(NO_2)(SO_2Cl)$: [97°]; tables.

Amide $C_6H_3Br(NO_2)(SO_2NH_2)$. [215°].

Bromo-nitro-benzene-sulphonic acid $C_6H_3Br(NO_2)(SO_3H)$ [1:3:6]. Formed by heating nitro-diazo-benzene-sulphonic acid (1:3:6) with HBr (Limpricht, *B.* 18, 2186).

Chloride: [75°], large yellow tables.

Amide: [166°], small white tables.

Bromo-nitro-benzene sulphonic acid $C_6H_3Br(NO_2)(SO_3H)$ [1:4:3]. Formed by nitrating bromo-benzene *m*-sulphonic acid (Berndsen, *A.* 177, 95; Thomas, *A.* 186, 124). Reduced to amido-benzene *o*-sulphonic acid. Exchange of NO_2 for Br gives *p*-di-bromo-benzene sulphonic acid.—$AgA'1\frac{1}{2}$aq.—$BaA'_2$3aq. S. 2·4 at 7°.—$CaA'_2$6aq.—KA'.—NH_4A'.—$PbA'_2$3aq.

Chloride $C_6H_3Br(NO_2)(SO_2Cl)$. [83°].

Amide $C_6H_3Br(NO_2)(SO_2NH_2)$. [170°].

Bromo-nitro-benzene sulphonic acid $C_6H_3Br(NO_2)(SO_3H)$ [1:2:4]. Formed by nitrating bromo-benzene *p*-sulphonic acid (Goslich, *A.* 180, 93; Limpricht, *B.* 8, 456). Formed also by sulphonating *o*-bromo-nitro-benzene (A. a. P.; Andrews, *B.* 13, 2127). Reduction by HI at 120° gives amido-benzene *m*-sulphonic acid.—BaA'_2aq. S. (of BaA'_2) 1·71 at 15° (A.).—$BaA'_2 1\frac{1}{2}$aq. S. (of BaA'_2) 1·46 at 9° (G.).—$CaA'_2$2aq (A. a. P.).—$CaA'_2 2\frac{1}{2}$aq. S. (of CaA'_2) 4·71 at 9° (G.).—$CuA'_2 9\frac{1}{2}$aq.—KA'. S. 1·02 at 9° (G.). NH_4A'. S. 5·96 at 9°.—$PbA'_2$2aq.—$ZnA'_2$2aq.

Chloride $C_6H_3Br(NO_2)(SO_2Cl)$. [40°–50°] (A.); [57°] (G.).

Amide $C_6H_3Br(NO_2)(SO_2NH_2)$: [177°]; plates.

Bromo-nitro-benzene di-sulphonic acid $C_6H_2Br(NO_2)(SO_3H)_2$. From nitro-benzene *m*-sulphonic acid *via* di-nitro-benzene di-sulphonic acid and amido-nitro-benzene disulphonic acid (Limpricht, *B.* 8, 289). Trimetric tables (containing aq).

Di-bromo-nitro-benzene sulphonic acid $C_6H_2Br_2(NO_2)(SO_3H)$ [1:2:4:6]. From *o*-di-bromo-benzene sulphonic acid and fuming HNO_3 (Goslich, *A.* 186, 152). Reduction gives di-bromo-aniline sulphonic acid.—$BaA'_2$3aq. S. ·9 at 7°.—$CaA'_2$4aq.—$CaA'_2$6aq.—KA'.—NH_4A'.—$PbA'_2$3aq. S. ·8 at 11°.

Chloride $C_6H_2Br_2(NO_2)SO_2Cl$. [99°].

Amide $C_6H_2Br_2(NO_2)SO_2NH_2$. [211°].

Di-bromo-nitro-benzene sulphonic acid $C_6H_2Br_2(NO_2)(SO_3H)$ [1:4:3?:5]. From (1,4,5)-di-bromo-benzene sulphonic acid and HNO_3 (Borns, *A.* 187, 358; Hübner a. Williams, *A.* 167, 121). Hygroscopic prisms which blacken at 100°.—BaA'_2aq.—$BaA'_2 1\frac{1}{2}$aq. $BaA'_2 2\frac{1}{2}$aq.—$BaA'_2$6aq.—$BaA'_2$9aq.—$CaA'_2$3aq. CuA'_2aq.—KA'aq. KA'$2\frac{1}{2}$aq.—$NH_4A'\frac{1}{2}$aq.—$PbA'_2$2aq.—$PbA'_2$3aq. S. 10·3 at 10°.

Chloride $C_6H_2Br_2(NO_2)(SO_2Cl)$. Oil (?).

Amide $C_6H_2Br_2(NO_2)(SO_2NH_2)$. [178°].

Di-bromo-nitro-benzene sulphonic acid $C_6H_2Br_2(NO_2)(SO_3H)$ [1:3:4:5]. From *s*-di-bromo-benzene sulphonic acid and HNO_3 (Lenz, *A.* 181, 32). Tablets (containing *x*aq); not hygroscopic. By exchanging NO_2 for Br it is converted into (1,3,4,5)-tri-bromo-benzene sulphonic acid.—$BaA'_2 1\frac{1}{2}$aq. S. ·73 at 20°.—$BaA'_2$4aq.—$CaA'_2$3aq.—KA'aq. S. 1·09 at 20°.—NH_4A'.—$PbA'_2$5aq. S. ·120 at 20°.

Chloride $C_6H_2Br_2(NO_2)(SO_2Cl)$. [121°].

Amide $C_6H_2Br_2(NO_2)(SO_2NH_2)$. Blackens at 300°.

Di-bromo-nitro-benzene sulphonic acid $C_6H_2Br_2(NO_2)SO_3H$ [1:3:4:6] [above 200°]. Formed by nitrating $C_6H_3Br_2SO_3H$ [1:3:4] (Bässmann, *A.* 191, 235). Deliquescent needles or prisms (containing *x*aq).—KA'. S. 1·4 at 21·5°.—BaA'_2aq. S. (of BaA'_2) 1·06 at 24°.—$CaA'_2$6aq.—$PbA'_2$4aq.

Chloride $C_6H_2(NO_2)Br_2SO_2Cl$. [115·5°].

Amide $C_6H_2(NO_2)Br_2SO_2NH_2$. Minute tablets. Not melted at 240°.

Tri-bromo-nitro-benzene sulphonic acid $C_6HBr_3(NO_2)SO_3H$ 2aq [1:3:5:2:6]. [c. 100°]. Formed by nitrating $C_6H_2Br_3SO_3H$ (Langfurth, *A.* 191, 196; Reinke, *A.* 186, 282; Bässmann, *A.* 191, 216). Hygroscopic, monoclinic prisms. Conc. HCl at 180° gives H_2SO_4 and $C_6H_2Br_3(NO_2)$ [125°].—KA'. S. ·76 at 5° (B.); 1·33 at 11° (L.).—BaA'_2aq. S. (of BaA'_2) ·207 at 1·5° (B.); ·331 at 15° (L.). $BaA'_2 1\frac{1}{2}$aq.—$CaA'_2$2aq.—$PbA'_2$9aq. S. (of PbA'_2) ·63 at 7° (B.); ·93 at 10° (L.).—$PbA'_2 1\frac{1}{2}$aq.—PbA'_2PbO 7aq.—PbA'_2PbO 6aq. NH_4A'.

Chloride $C_6HBr_3(NO_2)SO_2Cl$. [145°].

Amide $C_6HBr_3(NO_2)SO_2NH_2$.

Tri-bromo-nitro-benzene sulphonic acid $C_6HBr_3(NO_2)(SO_3H)$ [1:2:3:4:5]. From (1,2,3,5)-tri-bromo-benzene sulphonic acid by nitration (Limpricht a. Lenz, *B.* 8, 1072, 1432; *A.* 181, 41). Laminæ.—$BaA'_2$4aq, S. ·074 at 18°.—$CaA'_2$3aq. S. 1·05 at 20°.—KA' aq. S. ·16 at 18°. NH_4A'aq. PbA'_2aq. S. ·14 at 20°.

Chloride $C_6HBr_3(NO_2)(SO_2Cl)$. [116°].

Amide $C_6HBr_3(NO_2)(SO_2NH_2)$. [202°].

Tri-bromo-nitro-benzene sulphonic acid $C_6HBr_3(NO_2)(SO_3H)$ [1:3:4:2:6]. [125°] or, anhydrous, [141°]. From (1,2,4,5)-tri-bromo-benzene sulphonic acid and HNO_3 (Spiegelberg, *A.* 197, 284) columns (containing 3aq).—AgA'aq. S. (of AgA') ·45 at 7°. $BaA'_2$3aq. S. (of BaA'_2). ·669 at 9°.—$CaA'_2 4\frac{1}{2}$aq. S. (of CaA'_2) 1·95 at 8°. KA'. S. 1·19 at 8°.—NH_4A'. S. 1·68 at 6·5°.—$PbA'_2$6aq. S. (of PbA'_2) ·853 at 7°.

Chloride $C_6HBr_3(NO_2)(SO_2Cl)$. [143°].

Amide $C_6HBr_3(NO_2)(SO_2NH_2)$. Blackens at 250°.

Tri-bromo-di-nitro-benzene sulphonic acid $C_6Br_3(NO_2)_2SO_3H$ [1:3:5:2:4:6]. [216°]. From $C_6H_2Br_3SO_3H$ and conc. HNO_3 at 100° (Bässmann, *A.* 191, 239). Colourless columns (containing 3aq). Not hygroscopic, but v. sol. water, sol. alcohol.—With water at 230° it gives $C_6HBr_3(NO_2)_2$ and H_2SO_4. Reduced by Sn and HCl to $C_6H_2Br(NH_2)_2SO_3H$.—NH_4A'aq.—KA'aq. S. (of KA') ·48 at 24°.—$BaA'_2$9aq. S. (of BaA'_2) ·83 at 21°.—$CaA'_2 7\frac{1}{2}$aq. $PbA'_2$9aq. S. (of PbA'_2) 1·02 at 19·5°.

Chloride $C_6Br_3(NO_2)_2SO_2Cl$. [203°].

Amide $C_6Br_3(NO_2)_2SO_2NH_2$. [260°].

Tetra-bromo-nitro-benzene sulphonic acid $C_6Br_4(NO_2)SO_3H$ [1:2:3:5:4:6]. Got by nitrating $C_6HBr_4SO_3H$. Crusts of needles (containing 4aq). V. sol. alcohol and water (Beckurts, *A.* 181, 220; Langfurth, *A.* 191, 202). With conc. HCl at 200° it gives $C_6HBr_4(NO_2)$ and H_2SO_4.—KA'$1\frac{1}{2}$aq. S. (of KA') ·57 at 10·5°.—$BaA'_2$9aq. S. (of BaA'_2) ·36 at 11° (B.); ·100 at 14·5° (L.).—NH_4A'aq. S. (of NH_4A') 1·01 at 11°.—$CaA'_2$8aq. S. (of CaA'_2) ·16 at 6°.—$PbA'_2$9aq. S. (of PbA'_2) ·06 at 6°.

Chloride $C_6Br_4(NO_2)SO_2Cl$: [147·5°]; tablets.

Amide: crystalline powder.

Tetra-bromo-nitro-benzene sulphonic acid $C_6Br_4(NO_2)SO_3H$ [1:2:3:4:5:6]. [173°]. From c-tetra-bromo-benzene sulphonic acid and HNO_3 (Spiegelberg, *A.* 197, 297). Slender needles (containing aq).—$BaA'_2$4aq. S. (of BaA'_2) ·22 at 12°.—BaA'_2 9aq.—CaA'_2 aq. S. (of CaA'_2) 2·8 at 13°.—KA'aq. S. (of KA') ·17 at 11°.—NH_4A'. S. ·46 at 11°.—$PbA'_2$2aq. S. ·042 at 11°.

Chloride $C_6Br_4(NO_2)(SO_2Cl)$: [173°]; prisms.

Amide $C_6Br_4(NO_2)(SO_2NH_2)$. Blackens at 260°.

BROMO-NITRO-BENZOIC ACID

$C_6H_3Br(NO_2)CO_2H$ [1:4:3]. [141°]. Formed, together with the isomeride [250°] by nitrating *m*-bromo-benzoic acid (Hübner a. Ohly, *Z.* [2] 1, 547; 2, 241; *A.* 143, 230; 222, 102). Monoclinic prisms.—NaA'3aq.—NaA'2½aq.—KA'2aq.—$BaA'_2$4aq.—CaA'_2 2aq.—$MgA'_2$4aq.—PbA'_2.—CuA'_2.—AgA'.

Ethyl ether EtA': [55°]; monoclinic prisms.

Bromo-nitro-benzoic acid $C_6H_3Br(NO_2)CO_2H$ [1:3:5]. [161°]. S. ·057 at 11°. Formed from $C_6H_3(NH_2)(NO_2)CO_2H$, glacial acetic acid, HBr (S.G. 1·49), and nitrous acid gas (Hesemann a. Köhler, *A.* 222, 166). Long needles (from water, benzene, ether, or CS_2), whetstone-shaped crystals (from glacial acetic acid) or thin six-sided plates (from alcohol). — KA'½aq. — $BaA'_2$5½aq.—CaA'_2 aq.—MgA'_2 aq.—$ZnA'_2$4½aq.—$CdA'_2$4½aq.—SrA'_2.—AgA'.—PbA'_2.

Bromo-nitro-benzoic acid $C_6H_3Br(NO_2)CO_2H$ [1:3:6]. [164°]. Formed by oxidation of $C_6H_3Br(NO_2)Me$ by dilute HNO_3 (Scheufelen, *A.* 231, 173). V. sol. ether and dilute alcohol. Sl. sol. water. Reduced by Sn and HCl to *m*-bromo-aniline, CO_2 going off.—AgA'.

Bromo-nitro-benzoic acid $C_6H_3Br(NO_2)(CO_2H)$ [1:4:6]. [180°]. From $C_6H_3MeBr(NO_2)$ [1:2:5] and dilute HNO_3 (Scheufelen, *A.* 231, 181) or by nitrating *o*-bromo-benzoic acid (Burghard, *B.* 8, 560). Almost insol. cold water, sl. sol. hot water, v. sol. ether and dilute alcohol. Alcoholic NH_3 at 130° gives *p*-nitro-aniline and (1, 4, 6)-amido-nitro-benzoic acid.—$BaA'_2$5½aq.

Ethyl ether EtA': [66°]; needles.

Bromo-nitro-benzoic acid

$C_6H_3Br(NO_2)CO_2H$ [1:2:4]. [199°]. Formed by nitration of *p*-bromo-benzoic acid [248] (Hübner, *A.* 143, 248; Raveill, *A.* 222, 177) and by oxidation of the corresponding bromo-nitro-toluene (Scheufelen, *A.* 231, 183). Long needles (from water) or plates (from dilute alcohol); v. sol. ether, sl. sol. water. Reduction gives *m*-amido-benzoic acid.

Salts.—AgA'.—$BaA'_2$4aq.—$MgA'_2$6aq.

Ethyl ether EtA': [74°]; prisms.

Bromo-nitro-benzoic acid

$C_6H_3Br(NO_2)CO_2H$ [1:2:3]. [250°]. From *m*-bromo-benzoic acid by nitration. Separated from its isomeride [141°] by being less soluble in water (Hübner, *A.* 143, 234; *A.* 222, 101). Monoclinic octahedra (from ether).—NaA'aq.—$BaA'_2$4aq.—$MgA'_2$6aq.

Ethyl ether EtA': [80°]; prisms.

Di-bromo-nitro-benzoic acid

$C_6H_2Br_2(NO_2)CO_2H$ [3:4:2or6:1]. [162°]. From di-bromo-benzoic acid [230°] by nitration (E. F. Smith, *A.* 222, 188). Colourless needles; reduction gives anthranilic acid.

Salts.—PbA'_2.—NaA'3aq.—KA'.—BaA'_2aq.—$CaA'_2$3½aq.—MgA'_2.

Di-bromo-nitro-benzoic acid

$C_6H_2Br_2(NO_2)(CO_2H)$. [162°]. Formed by nitrating the di-bromo-benzoic acid [223°-227°] obtained by brominating benzoic acid (Angerstein, *A.* 158, 13). Needles (from water). Reduction gives di-bromo-amido-benzoic acid [196°] and then anthranilic acid.—NaA'3aq.—$BaA'_2$2aq. This acid is perhaps identical with the preceding.

Di-bromo-nitro-benzoic acid

$C_6H_2Br_2(NO_2)CO_2H$ [3:5:2:1]. [233°]. Formed by nitration of $C_6H_3Br_2CO_2H$ (Hesemann a. Köhler, *A.* 222, 173). Long colourless needles; may be sublimed.—$BaA'_2$4aq.—CaA'_2.—AgA'.—KA'.

BROMO-NITRO-*o*-BENZYL-PHENOL

$C_{13}H_{10}BrNO_3$. [105°-110°]. From potassium nitro-*o*-benzyl-phenol sulphonic acid and Br (Rennie, *C. J.* 49, 410). Yellow scales (from alcohol).—KA'.

Bromo-nitro-*p*-benzyl-phenol

$Ph.CH_2.C_6H_2Br(NO_2)OH$ [1:3:5:4]. [65°].

Formation.—1. From potassic bromo-benzyl-phenol sulphonate and dilute HNO_3 (1:1) (Rennie, *C. J.* 41, 223).—2. From potassic nitro-benzyl-phenol sulphonate, $C_{13}H_{11}O_2$, and Br.—3. From nitro-benzyl-phenol, $C_{13}H_{11}O_3$, and Br.—4. From benzyl-phenol by first brominating and then nitrating.

Properties.—Crystalline scales (from alcohol).—KA'. Red scales. HNO_3 oxidises it to bromo-di-nitro-phenol, $C_6H_2Br(NO_2)_2OH$ [1:2:3:5] [118°].

BROMO-NITRO-BUTANE $C_4H_8BrNO_2$ *i.e.* $C_3H_7.CHBr(NO_2)$. (181° cor.). From nitro-butane, potash, and Br (Züblin, *B.* 10, 2085). The three following compounds are prepared in a similar way (Z.).

Di-bromo-nitro-butane $C_3H_7CBr_2(NO_2)$. (204° cor.).

Bromo-di-nitro-butane $C_3H_7CBr(NO_2)_2$. Not volatile.

Bromo-di-nitro-iso-butane

$(CH_3)_2CH.CBr(NO_2)_2$. [38°]. Solid resembling camphor. Volatile with steam. Readily decomposed by alkalis forming dinitro-isobutane.

BROMO-*m*-NITRO-CINNAMIC ACID

[3:1] $C_6H_4(NO_2).C_2HBr.CO_2H$. [212°]. Formed by heating the dibromide of *m*-nitro-benzylidene-malonic acid (Stuart, *C. J.* 49, 361).

Bromo-*p*-nitro-cinnamic acid

[4:1] $C_6H_4(NO_2).C_2HBr.CO_2H$. [146°]. V. sol. alcohol, ether, chloroform. Sl. sol. hot CS_2. More sol. in cold water than its isomeride [205°].

Salts.—BaA'_2. Boiled with water gives nitro-phenyl-acetylene, CO_2 and $BaBr_2$.

Ethyl ether EtA'. [63°]. Prisms. From $C_6H_4(NO_2)CHBr.CHBr.CO_2Et$ and alcoholic KOH (C. L. Müller, *A.* 212, 131).

Bromo-*p*-nitro-cinnamic acid

[4:1] $C_6H_4(NO_2).C_2HBr.CO_2H$. [205°]. Slender silky needles (from water). Sl. sol. cold water, insol. cold CS_2. V. sol. alcohol, ether, chloroform, or benzoline.

Salt.—BaA'_2. Decomposed by boiling into nitro-phenyl-acetylene, CO_2 and $BaBr_2$.

Ethyl ether EtA'. [93°]. Needles. From di-exo-bromo-*p*-nitro-phenyl-propionic ether by alcoholic KOH (C. L. Müller, *A.* 212, 131).

Di-bromo-*p*-nitro-cinnamic acid

[4:1] $C_6H_4(NO_2).CBr:CBr.CO_2H$. [c. 180°]. From *p*-nitro-phenyl-propiolic acid and Br (Drewson, *A.* 212, 157).

Ethyl ether EtA'. [86°]. V. sol. benzene, chloroform or glacial HOAc, sl. sol. benzoline.

BROMO-NITRO-CINNAMIC ALDEHYDE $C_6H_4(NO_2).CH:CBr.CHO$. [97°]. Long yellowish needles. Formed together with the isomeride [136°] by nitration of *a*-bromo-cinnamic aldehyde.

Phenyl-hydrazide. [131°]. Large yellow plates (Zincke a. Hagen, *B.* 17, 1816).

Bromo-nitro-cinnamic aldehyde $C_6H_4(NO_2).CH:CBr.CHO$. [136°]. Yellowish needles. Formed as above.

Phenyl-hydrazide. [151°]; red crystalline solid, sl. sol. alcohol (Z. a. H.).

DI-BROMO-NITRO-*o*-CRESOL $C_6H(CH_3)(NO_2)(Br)_2(OH)$ [1:4:*x*:2] [92°]. Formed by bromination of nitro-*o*-cresol $C_6H_3(CH_3)(NO_2)(OH)$ [1:4:2]. Yellowish needles. V. sol. alcohol and ether, nearly insol. water (Nölting a. Collin, *B.* 17, 270).

Di-bromo-nitro-*p*-cresol $C_6HMe(NO_2)(OH)Br_2$ [1:2:4:?:?]. [83°]. From aqueous nitro-cresol, [78°], and bromine-water. Long yellow needles (from alcohol). Insol. cold water, v. sl. sol. hot water, v. sol. alcohol or ether (E. Knecht, *A.* 215, 89; *B.* 15, 1071).

Salts.—$C_6HMe(NO_2)(ONa)Br_2 2\frac{1}{2}aq$. Red needles (from alcohol).—$C_6HMe(NO_2)(OK)Br_2aq$.

DI-BROMO-NITRO-CUMENE $C_6H_5.CHBr.CBr(NO_2).CH_3$. *Di-bromo-nitro-phenyl-propylene.* [77°–78·5°]. From $Ph.CH:C(NO_2).CH_3$ and Br (Priebs, *A.* 225, 362). Colourless prisms (from light petroleum). Not decomposed even by hot aqueous NaOH, thus differing markedly from the corresponding di-bromo-nitro-ethyl-benzene.

Bromo-nitro-ψ-cumene $C_6HMe_3Br(NO_2)$ [1:2:4:5:*x*]. [192°]. Formed by nitration of bromo-pseudo-cumene [73°] by fuming HNO_3. Needles. Sol. benzene, sl. sol. alcohol (Kelbe a. Pathe, *B.* 19, 1548).

Bromo-di-nitro-ψ-cumene $C_6Me_3Br(NO_2)_2$ [1:2:4:3:5:6]. [181°]. Formed by nitration of bromo-pseudo-cumene [1:2:4:3]. Long yellowish needles. Sl. sol. hot alcohol, nearly insol. cold (Kelbe a. Pathe, *B.* 19, 1551).

Bromo-di-nitro-ψ-cumene $C_6Me_3Br(NO_2)_2$ [1:2:4:5:3:6]. [214°]. Formed by nitration of bromo-pseudo-cumene [73°] with fuming HNO_3 and conc. H_2SO_4. Microscopic tables. Sol. benzene, sl. sol. hot alcohol, nearly insol. cold alcohol (Fittig, *A.* 147, 14; Kelbe a. Pathe, *B.* 19, 1548).

BROMO-NITRO-*iso*-CUMENOL $C_9H_{10}BrNO_3$ *i.e.* $C_6H_2(C_3H_7)Br(NO_2)(OH)$ [1:5:3:2]. *Bromo-nitro-isopropyl-phenol.* [33°]. From bromo-iso-propyl-phenol and HNO_3 (Fileti, *G.* 16, 123). Pale yellow needles (from dilute HOAc).

Bromo-nitro-iso-cumenol $C_6H_2PrBr(NO_2)(OH)$ [1:3:5:2]. [88°]. From nitro-isopropyl phenol and Br (F.). Nacreous tables (from dilute alcohol); volatile with steam.

BROMO-NITRO-CUMYL-PROPIONIC ACID $C_{12}H_{14}BrNO_4$ *i.e.* $C_6H_3(C_3H_7)(NO_2).CHBr.CH_2.CO_2H$. [127°]. From *o*-nitro-*eso*-propyl-cinnamic acid and HBr (Einhorn a. Hess, *B.* 17, 2020).

Di-bromo-nitro-cumyl-propionic acid $C_6H_3(C_3H_7)(NO_2).CHBr.CHBr.CO_2H$. [171°]. From *o*-nitro-*eso*-propyl-cinnamic acid and Br (Widman, *B.* 19, 260).

Di-bromo-nitro-cumyl-propionic acid. [184°]. From *m*-nitro-*eso*-propyl-cinnamic acid and Br (Widman, *B.* 19, 418).

BROMO-NITRO-CYMENE $C_{10}H_{12}BrNO_2$ *i.e.* $C_6H_2Me(C_3H_7)Br(NO_2)$ [1:4:3:*x*]. Formed by nitrating the bromo-cymene derived from thymol (Mazzara, *G.* 16, 193). Oil, volatile with steam.

Bromo-di-nitro-cymene $C_6HMePrBr(NO_2)_2$ [1:4:2?:?:?]. [98°]. Formed by nitrating bromo-cymene (229°). Monoclinic prisms (Gerichten, *B.* 11, 1092). May be identical with the following.

Bromo-di-nitro-cymene $C_6HMePrBr(NO_2)_2$ [1:4:3:?:?]. [94°]. Formed by nitrating the bromo-cymene derived from thymol (M.). Slender yellow needles.

Bromo-nitro-isocymene $C_6H_2(C_3H_7)(CH_3)(Br)(NO_2)$ [4:2:1:?]. [121°]. Long red needles. Prepared by nitration of (1:2:4)-bromo-isocymene (Kelbe, *B.* 15, 40).

Bromo-nitro-*m*-isocymene (?) $C_{10}H_{12}(NO_2)Br$. [83°]. From di-bromo-*m*-isocymene by nitration (Kelbe a. Czarnomski, *A.* 235, 281).

Bromo-di-nitro-isocymene $C_6H(C_3H_7)(CH_3)(NO_2)_2(Br)$. [55°]. Short thick needles. Prepared by nitration of (β)-bromo-isocymene (Kelbe, *B.* 15, 42).

BROMO-NITRO-ETHANE $C_2H_4BrNO_2$ *i.e.* $CH_3.CHBr(NO_2)$. (147°). Formed by dissolving nitro-ethane (*q.v.*) in aqueous caustic potash and adding bromine: $CH_3.CHK(NO_2) + Br_2 = CH_3.CHBr(NO_2) + KBr$ (Meyer a. Wurster, *B.* 6, 94; Tscherniak, *B.* 7, 916; *A.* 180, 126).—Pungent oil. Forms unstable salts.

Bromo-di-nitro-ethane $CH_3.CBr(NO_2)_2$. From Br and potassium dinitroethane (Ter Meer, *A.* 181, 15).—Oil, volatile with steam; decomposed by K_2CO_3 which forms $CH_3.CK(NO_2)_2$.

Di-bromo-tetra-nitro-ethane $CBr(NO_2)_2.CBr(NO_2)_2$. From ethylene bromide and fuming HNO_3, or from $C_2(NO_2)_4K_2$ and Br. Unstable liquid; forms with potash a compound $C_2Br_2(NO_2)_4 2KOH$, m. sol. hot water, which explodes at about 180°. Ammonium sulphide converts it into $C_2K_2(NO_2)_4$. SO_2 forms NH_3, HBr, and HCN. Aqueous K_2SO_3 forms yellow crystals $C_2(NO_2)_4K_2 3K_2SO_4$ (Villiers, *C. R.* 94, 1122; 98, 431).

Di-bromo-nitro-ethane $CH_3.CBr_2(NO_2)$. (165°). Formed by adding potash to a mixture of nitro-ethane (*q. v.*) and the calculated quantity of bromine (V. Meyer, *B.* 7, 1313). Indifferent oil, insol. KHO.

BROMO-NITRO-ETHENYL-NAPHTHYLENE-DIAMINE

$$C_{10}H_4Br(NO_2)\Big\langle{}^{N}_{NH}\Big\rangle C.CH_3\left[4:x:{}^{2}_{1}\right].\quad [242°].$$

Formed by nitration of ethenyl-(4:2:1)-bromo-naphthylene-diamine (Prager, *B.* 18, 2162). Yellow needles sl. sol. alcohol, v. sol. HNO_3Aq.

ωα-DI-BROMO-*o*-NITRO-ETHYL-BENZENE $C_8H_7Br_2NO_2$ *i.e.* [2:1] $C_6H_4(NO_2).CHBr.CH_2Br$. *o-nitro-styrene dibromide.* [52°]. From *o*-nitro-styrene and Br (Einhorn, *B.* 16, 2213).

ωα-Di-bromo-*m*-nitro-ethyl-benzene [3:1] $C_6H_4(NO_2).CHBr.CH_2Br$. [79°]. From *m*-nitro-styrene and Br (Prausnitz, *B.* 17, 598).

ωα-Di-bromo-*p*-nitro-ethyl-benzene [4:1] $C_6H_4(NO_2).CHBr.CH_2Br$. [73°]. From *p*-nitro-styrene and Br (Basler, *B.* 16, 3006).

ωα-Di-bromo-ω-nitro-ethyl-benzene $C_6H_5.CHBr.CHBrNO_2$. [86°]. From ω-nitro-phenyl-ethylene and Br (Erdmann, *B.* 17, 414). Also from ω-nitro-ethyl-benzene and Br (Priebs, *A.* 225, 341). Monoclinic crystals, $a:b:c = 1·257:1:1·396$; $L = 83°\ 54'$. Cold aqueous NaOH gives bromo-nitro-styrene.

ωα-**Di-bromo-*ωo*-di-nitro-ethyl-benzene** [2:1] $C_6H_4(NO_2).CHBr.CHBrNO_2$. [91°]. From *ωo*-di-nitro-phenyl-ethylene and Br (Priebs, *A.* 225, 352). White needles, v. sl. sol. ligroïn.

ωα-**Di-bromo-*ωp*-di-nitro-ethyl-benzene** [4:1] $C_6H_4(NO_2).CHBr.CHBrNO_2$. [103°]. From *ωp*-di-nitro-phenyl-ethylene and Br (P.). Plates.

DI-BROMO-NITRO-ETHYLENE $C_2HBr_2(NO_2)$. [112°]. From sodium tri-nitro-resorcin $C_6H(NO_2)_3(OH)(ONa)$ in aqueous solution, and bromine vapour (Merz a. Zetter, *B.* 12, 2046). Prisms (from $CHCl_3$); does not combine with Br. Zn and HCl give ethylamine.

DI-BROMO-DI-NITRO-FLUORESCEÏN $C_{20}H_8Br_2(NO_2)_2O_5$. From di-bromo-fluoresceïn and HNO_3, or from di-nitro-fluoresceïn and Br. Yellow needles; is not fluorescent.

Acetyl derivative [256°] (Baeyer, *A.* 183, 61).

BROMO-NITROFORM *v.* BROMO-TRI-NITRO-METHANE.

BROMO-NITRO-HYDROCINNAMIC ACID *v.* BROMO-NITRO-PHENYL-PROPIONIC ACID.

BROMO NITRO-MESITYLENE $C_9H_{10}BrNO_2$ *i.e.* $C_6HBrMe_3(NO_2)$. [54°]. Formed by nitrating bromo-mesitylene (Fittig a. Storer, *A.* 147, 7).

Bromo-di-nitro-mesitylene $C_6BrMe_3(NO_2)_2$. [194°]. From di-bromo-mesitylene by fuming HNO_3. Needles (Süssenguth, *A.* 215, 248).

BROMO-NITRO-METHANE $CH_2Br(NO_2)$. (144°). Formed by the action of bromine on sodium nitro-methane (Tscherniak, *B.* 7, 916; *A.* 180, 128 *v.* NITRO-METHANE). Pungent oil. The bromine and nitroxyl render its hydrogen displaceable by sodium: it is a strong acid.

Bromo-di-nitro-methane $CHBr(NO_2)_2$. From di-bromo-di-nitro-methane and alcoholic KOH (Villiers, *Bl.* [2] 37, 452; Losanitsch, *B.* 16, 51); or from (α)-di-bromo-camphor and conc. HNO_3 (Kachler a. Spitzer, *M.* 4, 558). Oil.

Salt.—$CKBr(NO_2)_2$: S.G. $\frac{14}{}$ 1·25; triclinic crystals which explode at about 147°. Reduction by sodium-amalgam gives HCN, HBr, and NH_3 (Villiers, *Bl.* [2] 41, 282). Ammonium sulphide gives di-nitro-methane.

Bromo-tri-nitro-methane $CBr(NO_2)_3$. *Bromo-nitroform.* [about 12°]. S.G. 2·8. From nitroform and Br in sunlight; or from mercuric nitroform and Br (Schischkoff, *A.* 119, 247). Decomposes at 140°, but volatile with steam.

Di-bromo-nitro-methane $CHBr_2(NO_2)$. (155°–160°). Formed by adding bromine to potassic bromo-nitro-methane:

$CHKBr(NO_2) + Br_2 = CHBr_2(NO_2) + KBr$.

Bromopicrin, insoluble in potash, is formed at the same time (Tscherniak, *A.* 180, 130). Very pungent oil, volatile with steam, soluble in caustic soda.

Di-bromo-di-nitro-methane $CBr_2(NO_2)_2$. [c. 0°]. Formed by the action of conc. HNO_3 on tri-bromo-aniline, ethylene bromide, bromo-phenol, or di-bromo-*p*-toluidine (Losanitsch, *B.* 15, 472; Villiers, *Bl.* [2] 37, 452). Greenish-yellow, pungent oil, volatile with steam. Alkalis form salts of bromo-di-nitro-methane.

Tri-bromo-nitro-methane $CBr_3(NO_2)$. *Bromo-picrin* [10°]. S.G. $\frac{12}{}$: 2·811.

Formation.—From nitro-methane, bromine, and KOH (V. Meyer a. Tscherniak, *A.* 180, 122).

Preparation.—CaO (4 pts.), H_2O (50 pts.), Br_2 (6 pts.) and picric acid (1 pt.) are mixed in the order named and the product is distilled (Stenhouse, *P. M.* [4] 8, 36; Groves a. Bolas, *A.* 155, 253; *C. J.* 23, 153).

Properties.—Pungent prisms, may be distilled *in vacuo*. Converted by Br into CBr_4.

BROMO-DI-NITRO-METHYL-ANILINE $C_6H_2Br(NO_2)_2NHMe$ [1:3:5:6]. [147°]. From di-nitro-methyl-aniline and Br. Yellow crystals; boiling aqueous KOH gives bromo-di-nitro-phenol (Norton a. Allen, *B.* 18, 1996).

Bromo-nitro-di-methyl-aniline $C_6H_3Br(NO_2)NMe_2$ [4:3:1]. [72°]. Long crystals. Formed together with other products by the action of nitrous acid upon *p*-bromo-di-methyl-aniline (Koch, *B.* 20, 2460).

BROMO-DI-NITRO-METHYL-DI-PHENYL-AMINE $C_{13}H_{10}NBr(NO_2)_2$. [194°]. Light yellow tables. Formed by bromination of di-nitro-methyl-di-phenyl-amine (Leymann, *B.* 15, 1236).

BROMO-NITRO-NAPHTHALENE $C_{10}H_6Br(NO_2)$ [1:4]. [85°]. From (α) bromo-naphthalene and HNO_3. Yellow needles. PBr_5 gives $C_{10}H_6Br_2$ [81°] (Jolin, *Bl.* [2] 28, 515).

Bromo-nitro-naphthalene $C_{10}H_6Br(NO_2)$ [1:1' or 4']. [122·5°]. S. (93 p.c. alcohol) ·337 at 15·7°. From (α)-nitro-naphthalene and bromine (Guareschi, *A.* 222, 291). Yellow needles (from alcohol). $KMnO_4$ gives bromo-phthalic acid [174°–176°].

Bromo-nitro-naphthalene $C_{10}H_6Br(NO_2)$ [3:1]. [131°]. From (2,4,1)-bromo-nitro-(α)-naphthyl-amine by the diazo- reaction (Liebermann a. Scheiding, *A.* 183, 262; Meldola, *C. J.* 47, 508). Straw-coloured needles. Exchange of NO_2 for Br gives (1,3)-di-bromo-naphthalene [64°].

Bromo-nitro-naphthalene $C_{10}H_6Br(NO_2)$ [1:3]. [132°]. From (α)-naphthylamine by bromination, nitration, diazotisation &c. (Liebermann, *B.* 8, 1108; *A.* 183, 262). Yellow needles; Sn and HCl give (β)-naphthylamine.

Bromo-di-nitro-naphthalene $C_{10}H_5Br(NO_2)_2$. [170°]. Long glistening needles. Formed together with the following isomeride by nitration of (α)-bromo-naphthalene with fuming HNO_3 (1·5). Not attacked by boiling with aqueous NaOH. On oxidation with dilute HNO_3 it gave a small quantity of (α)-nitro-phthalic acid (Merz a. Weith, *B.* 15, 2710).

Bromo-di-nitro-naphthalene $C_{10}H_5Br(NO_2)_2$. [143°]. Tables or prisms. Formed as above. Not attacked by boiling aqueous NaOH. On oxidation with dilute HNO_3 it gave a little (α)-nitro-phthalic acid (Merz a. Weith, *B.* 15, 2710).

Bromo-tetra-nitro-naphthalene $C_{10}H_3Br(NO_2)_4$. [190°]. Needles. S. (benzene at 18°) 3·7. Formed by further nitration of bromo-di-nitro-naphthalene [170°] by heating with a mixture of HNO_3 and H_2SO_4. It dissolves in caustic alkalis forming tetra-nitro-naphthol. NH_3 converts it into tetra-nitro-naphthylamine, and aniline gives the phenyl derivative of the latter. On oxidation with dilute HNO_3 it gives

di-nitro-phthalic acid [227°] (Merz a. Weith, *B.* 15, 2712).

Bromo-tetra-nitro-naphthalene $C_{10}H_3Br(NO_2)_4$. [245°]. White glistening needles. Nearly insol. ordinary solvents. Formed by nitration of bromo-di-nitro-naphthalene [143°] with a mixture of HNO_3 and H_2SO_4. It is attacked by alkalis with difficulty. NH_3 converts it into tetra-nitro-naphthylamine and aniline gives the phenyl derivative of the latter. On oxidation with dilute HNO_3 it gives di-nitro-phthalic acid [200°] (Merz a. Weith, *B.* 15, 2718).

Di-bromo-nitro-naphthalene $C_{10}H_5Br_2(NO_2)$. [96·5°–98°]. One of the products of action of Br on nitro-naphthalene. Small yellow needles (from alcohol) (Guareschi, *A.* 222, 286).

Di-bromo-nitro-naphthalene $C_{10}H_5Br_2(NO_2)$ [1:4:1′]. [116·5°]. From (1,4)-di-bromo-naphthalene and HNO_3 (S.G. 1·4) in the cold (Jolin, *Bl.* [2] 28, 515). PCl_5 gives tri-bromo-naphthalene [85°].

Di-bromo-nitro-naphthalene $C_{10}H_5Br_2(NO_2)$. [100°–105°]. From di-bromo-naphthalene [68°] and HNO_3 (S.G. 1·4) (Canzoneri, *G.* 12, 427).

Tri-bromo-di-nitro-naphthalene $C_{10}H_3Br_3(NO_2)_2$. From (1, 2, 4)-tri-bromo-naphthalene and fuming HNO_3 (Prager, *B.* 18, 2164).

BROMO - NITRO - (α) - NAPHTHOIC ACID $C_{10}H_5Br(NO_2)CO_2H$ [1:4:4′]. [260°]. Formed by nitration of bromo-(α)-naphthoic acid [246°]. Small yellowish prisms (from alcohol). Its ammonium salt forms glistening plates, sl. sol. cold water (Ekstrand, *B.* 19, 1135).

BROMO-NITRO-(α)-NAPHTHOL $C_{10}H_5Br(NO_2)(OH)$ [2:4:1]. [136°]. From (2, 4, 1)-bromo-nitro-acetyl-(α)-naphthylamine and conc. NaOH. Silky needles (from alcohol); oxidation gives phthalic acid.

Salts.—$C_{10}H_5Br(NO_2)(ONa)$aq: red needles. —$(C_{10}H_5Br(NO_2)O)_2Ba$ 3aq.

Methyl ether $C_{10}H_5Br(NO_2)(OMe)$. [115°]. Pale yellow silky needles (Meldola, *C. J.* 47, 497).

Bromo-nitro-(α)-naphthol $C_{10}H_5Br(NO_2)OH$. [142°]. From acetyl-bromo-(α)-naphthylamine by nitration and saponification (Biedermann a. Remmers, *B.* 7, 538).

BROMO-NITRO-(α)-NAPHTHYLAMINE $C_{10}H_5Br(NO_2)(NH_2)$ [2:4:1]. [197°]. From the acetyl derivative by dissolving in conc. H_2SO_4 and ppg. with water. Orange needles; gives phthalic acid on oxidation (Meldola, *C. J.* 47, 497; 43, 9).

Acetyl derivative $C_{10}H_5Br(NO_2)(NHAc)$. [225°]. From acetyl-(α)-naphthylamine by nitration and bromination. Pale ochreous needles.

Bromo-nitro-(α)-naphthylamine $C_{10}H_5Br(NO_2)(NH_2)$ [4:2:1]. [200°]. From acetyl-(α)-bromo-(α)-naphthylamine by nitration and saponification (Liebermann a. Scheiding, *A.* 183, 258). Oxidised by dilute HNO_3 to phthalic acid. Elimination of NH_2 gives bromo-nitro-naphthalene [132°]. Conc. HBrAq at 130° gives (1, 2, 4)-tri-bromo-naphthalene.

Acetyl derivative $C_{10}H_5Br(NO_2)(NHAc)$. [232°].

DI-BROMO-NITRO-ORCIN $C_7H_5Br_2NO_4$ *i.e.* $C_6MeBr_2(NO_2)(OH)_2$. [112°]. From (β)-nitro-orcin and Br. Yellow laminæ (from alcohol).—$Ba(C_7H_4Br_2NO_4)_2$ 2aq: red needles (Weselsky, *B.* 7, 444).

BROMO-NITRO-o-OXY-BENZOIC ACID $C_6H_2Br(NO_2)(OH)CO_2H$ [5:3:2:1]. *Bromo-nitro-salicylic acid.* [175°]. Yellow needles. Formed by nitration of bromo-salicylic acid in acetic acid solution.—A'_2Ca *x*aq: V. sol. water.—A'_2Ba: yellow needles.—$C_6H_2Br(NO_2)<\begin{smallmatrix}CO.O\\O\end{smallmatrix}>Ba$ 2aq: red crystals.—$C_6H_2Br(NO_2)<\begin{smallmatrix}CO.O\\O\end{smallmatrix}>Pb$: nearly insoluble pp. (Lellmann a. Grothmann, *B.* 17, 2729).

Bromo-nitro-o-oxy-benzoic acid $C_6H_2Br(NO_2)(OH)CO_2H$ [3:5:2:1]. [222°]. Colourless needles. V. sol. alcohol, ether, and hot water. Formed by bromination of nitro-salicylic acid in acetic acid solution.

Salts.—A'_2Ba 4aq: long yellow needles.—A'_2Ca 6aq: yellow prisms (Lellmann a. Grothmann, *B.* 17, 2724).

Bromo-nitro-o-oxy-benzoic acid. *Methyl derivative* $C_6H_2Br(NO_2)(OMe)(CO_2H)$. From methyl bromo-isopropyl-phenyl oxide and HNO_3 (S.G. 1·3) (Peratoner, *G.* 16, 420). A di-bromo-nitro-o-oxy-benzoic acid is also formed.

Bromo-nitro-p-oxy-benzoic acid. *Methyl derivative* $C_6H_2Br(NO_2)(OMe)(CO_2H)$ [1:3:2:5]. [182°]. *Bromo-nitro-anisic acid.* Formed by nitrating bromo-anisic acid.

Ethyl ether EtA′. [85°]: needles (Balbiano, *G.* 14, 241).

DI-BROMO-DI-NITRO-DI-OXY-DI-PHENYL SULPHONE $C_{12}H_6Br_2N_2SO_8$ *i.e.* $(C_6H_2(NO_2)(OH)Br)_2SO_2$. [285°]. From di-nitro-di-oxy-di-phenyl sulphone in CS_2 and Br (Annaheim, *B.* 9, 660). Yellowish needles. — $C_{12}H_4Na_2Br_2N_2SO_8$ 2aq: orange needles.

BROMO-NITRO-OXY-PIPERIDINE-ν-CARBOXYLIC ETHER $C_5H_7(Br)(NO_2)(OH)N.CO_2Et$ [157°]. Colourless prisms; sol. alcohol. Formed by the action of Br in HOAc on nitro-dehydro-piperidine-ν-carboxylic ether (Schotten, *B.* 16, 646).

BROMO-NITRO-PHENANTHRENE *v.* PHENANTHRENE.

BROMO-o-NITRO-PHENOL $C_6H_3Br(NO_2)(OH)$ [1:4:3]. [44°]. Formed, together with the following body [88°] by boiling (1, 3, 4)-bromo-di-nitro-benzene with aqueous KOH (Laubenheimer, *B.* 11, 1160). Prisms; volatile with steam.—NaA′: scarlet needles.—BaA'_2 aq: red needles, sl. sol. water.—CaA'_2 2aq. AgA′.

Bromo-o-nitro-phenol $C_6H_3Br(NO_2)(OH)$ [1:3:4]. [88°].

Formation.—1. From *p*-bromo-phenol and HNO_3 (Hübner a. Brenken, *B.* 6, 170; Körner, *G.* 4, 388).—2. From o-nitro-phenol (45g.) and Br (52g.) (Brunck, *Z.* 1867, 203).—3. From bromo-di-nitro-phenol (*v. sup.*).

Properties.—Yellow monoclinic laminæ (from alcohol) $a:b:c = 2·941:1:1·625$. $\beta = 64°\ 2'$ (Arzruni, *Z. Kryst.* 1, 436); may be sublimed; v. sol. alcohol and ether, slightly volatile with steam. Reduced by Sn and HCl to bromo-amido-phenol (Schütt, *J. pr.* [2] 32, 61).

Salts.—$Na(C_6H_3BrNO_3)$: red needles with golden-green lustre, v. sol. water.—KA′ 2aq.—BaA'_2.—AgA′.

Methyl ether $C_6H_3Br(NO_2)OMe$. [88°]. From the silver salt and MeI by boiling; or from the potassium salt, MeOH and MeI at 110°. Needles. V. sol. hot alcohol or hot ether, v. sl. sol. water (Staedel, *A.* 217, 55; *B.* 11, 1750).

Ethyl ether $C_6H_3Br(NO_2)OEt$. [43°] (S.); [47°] (H.). From the potassium salt, EtI and alcohol at 100°. Formed also by nitrating *o*-bromo-phenetol.

Benzyl derivative $C_6H_3Br(NO_2)(OC_7H_7)$. [84°]. Yellow needles. Insol. water, v. sol. alcohol and glacial acetic acid, sl. sol. benzene, ether or chloroform (Roll a. Hölz, *J. pr.* [2] 32, 57). Reduced to bromo-amido-phenol, when treated with Sn and HCl, benzyl chloride splitting off.

Bromo-*m*-nitro-phenol $C_6H_3(Br)(NO_2)(OH)$ [?:3:1]. [147°] (L.); [110°] (P.). Prepared by bromination of *m*-nitro-phenol (Pfaff, *B.* 16, 612; Lindner, *B.* 18, 612). Yellow needles. Sublimable. Sl. sol. hot water, CS_2 and petroleum-ether, insol. cold water. On reduction with tin and HCl it gives *m*-amido-phenol, the Br atom being eliminated.—KA′ 2aq: red crystals, sol. water and alcohol.—NaA′ aq: yellowish-red crystals, sol. water and alcohol.—BaA'_2 4aq.

Methyl ether A′Me: [104°]; white needles, v. sol. alcohol and ether, on reduction with tin and HCl it gives *m*-anisidine.

Ethyl ether EtA′. [57°]: prisms.

Bromo-*p*-nitro-phenol $C_6H_3Br(NO_2)(OH)$ [1:3:6]. [102°]. Formed by brominating *p*-nitro-phenol (Brunck, *Z.* 1867, 201). Satiny needles (from ether or alcohol); m. sol. water.—$Ba(C_6H_3BrNO_3)_2$ 6aq: orange needles, m. sol. water.

Methyl ether MeA′. [106°]. From the potassium salt, MeI and MeOH at 110°. White needles (from alcohol). V. sol. hot alcohol or ether, m. sol. hot water (Staedel, *A.* 217, 66).

Ethyl ether EtA′. [98°] (S.); [55°] (H.). Formed like the preceding (S.). From *p*-nitro-phenetol and Br (Halloch, *B.* 14, 37). Yellow needles (from alcohol). V. sol. alcohol or ether.

Benzyl ether $C_6H_3Br(NO_2)(OC_7H_7)$. [126°]. Nearly colourless plates (from alcohol). Insol. water, sol. alcohol and ether (R. a. H.). Reduced by Sn and HCl to bromo-*p*-amido phenol and C_7H_7Cl.

Bromo-di-nitro-phenol $C_6H_2Br(NO_2)_2(OH)$ [1:3:5:4]. [86°] (K.); [71°] (Austen); [76°] (Armstrong). Formed by nitrating *p*-bromo-phenol in HOAc, or by brominating and nitrating *o*-nitro-phenol (Körner, *A.* 137, 205; Armstrong a. Prevost, *B.* 7, 922). Formed also by brominating di-nitro-phenol [64°] (Körner, *G.* 4, 305); and by boiling di-nitrated *p*-di-bromo-benzene with aqueous KNO_2 (Austen, *Am. S.* [3] 16, 46). Yellow monoclinic prisms, $a:b:c = 2·795:1:1·778$; $\beta = 67°\ 53'$ (Arzruni, *loc. cit.*). Water and Br at 100° change it into the isomeride [118°] (Armstrong, *C. J.* 28, 520). HNO_3 forms picric acid.

Salts.—NH_4A': silky red needles; sol. boiling water and alcohol.—NH_4A' aq.—BaA'_2: yellow needles, sol. hot water.—CuA'_2: short brown needles, insol. water.—KA′: long red needles, sl. sol. water.—AgA′.—CaA'_2 8aq.

Ethyl ether EtA′ [66°]: small needles, sol. alcohol and hot water; saponified by cold NaOHAq (Schoonmaker a. Van Mater, *Am.* 3, 187).

Bromo-di-nitro-phenol $C_6H_2Br(NO_2)_2(OH)$. [91·5°]. Formed by nitrating *m*-bromo-phenol, and also from di-bromo-di-nitro-phenol [117°] and boiling aqueous KOH (Körner, *G.* 4, 305). Prisms (from alcohol or ether). The K salt forms yellow needles.

Methyl ether MeA′ [109°].

Bromo-di-nitro-phenol $C_6H_2Br(NO_2)_2OH$ [1:3:5:6]. [118°].

Formation.—1. From (1,3,4)-di-nitro-phenol and Br (Laurent, *Rev. Scient.* 6, 65).—2. By nitrating *o*-bromo-phenol (Körner, *G.* 4, 394).—3. From *o*-nitro-phenol by bromination and nitration.—4. By boiling bromo-di-nitro-aniline [144°] with aqueous KOH (Körner).—5. By nitrating brominated phenol disulphonic acid or di-brominated phenol *p*-sulphonic acid (Armstrong a. Brown, *C. J.* 25, 861, 865).—6. By warming the isomeride [c. 76°] with Br and water (Armstrong, *C. J.* 28, 520).—7. From picric acid, water, and Br (Armstrong, *B.* 6, 650). 8. By nitrating tri-bromo-phenol (Armstrong a. Harrow, *C. J.* 29, 477).—9. From bromo-nitro-benzyl-phenol in HOAc by HNO_3: benzyl being displaced by NO_2 (Rennie, *C. J.* 41, 225).

Properties.—Yellow prisms. Needles (from alcohol).

Salts.—KA′aq: flat yellow needles, sl. sol. cold water.—KA′ 1½aq.—BaA'_2 3½aq.—BaA'_2 4aq.—BaA'_2 5aq: yellow needles, sl. sol. water.—CaA'_2 7aq.—CaA'_2 8aq.—CaA'_2 12aq.—NH_4A' 2aq.—NaA′ 1½aq.—PbA'_2 2aq.

Methyl ether MeA′. [48°]. From bromo-anisic acid and HNO_3. Yellow prisms, sol. alcohol and ether, insol. water (Balbiano, *G.* 14, 235).

Di-bromo-*o*-nitro-phenol $C_6H_2Br_2(NO_2)(OH)$ [1:3:5:6]. [117·5°].

Formation.—1. From *o*-nitro-phenol and Br (Brunck, *Z.* 1867, 203; Körner).—2. From (1,3,4,)-di-bromo-phenol by nitration (K.).—3. By nitrating di-bromo-phenol sulphonic acid (Armstrong a. Brown, *C. J.* 25, 863).

Properties.—Golden monoclinic prisms (from alcohol); $a:b:c = ·515:1:·591$; $\beta = 65°\ 23'$ (Arzruni, *Z. Kryst.* 1, 436). Volatile with steam; may be sublimed; v. sl. sol. water. Heated with bromine at 100° it gives some of the isomeride [141°] together with tetra-bromo-quinone and (1,3,6)-bromo-nitro-phenol (Ling, *C. J.* 51, 147).

Salt.—KA′: scarlet needles, v. sl. sol. cold water.

Methyl ether MeA′. [77°]. From the silver salt and MeI; alcoholic NH_3 converts it into di-bromo-nitro-aniline [127°] whence HNO_2 gives di-bromo-nitro-benzene [105°] (K.).

Ethyl ether EtA′. [46°]. From the silver salt, EtI and alcohol at 100° (Staedel, *A.* 217, 58). V. sol. benzene, alcohol or ether, insol. water.

Benzyl ether $C_6H_2Br_2(NO_2)(OC_7H_7)$. [65°]. Yellow crystals (from ether). Sol. benzene, chloroform, and glacial acetic acid, insol. water (R. a. H., *J. pr.* [2] 32, 57). Reduced by Sn and HCl to di-bromo-amido-phenol and benzyl chloride.

Di-bromo-*m*-nitro-phenol $C_6H_2Br_2(NO_2)OH$. [91°]. Formed by heating *m*-nitro-phenol (1

mol.) with bromine (2 mols.). Yellowish plates. V. sol. alcohol, sl. sol. water.

Salts.—KA′ aq: easily soluble orange-red needles.—AgA′: sparingly soluble red powder.—BaA'_2 6aq: very soluble red needles.

Ethyl ether $C_6H_2Br_2(NO_2)OEt$: [110°]: yellowish needles, sol. hot alcohol (Lindner, *B.* 18, 613).

Di-bromo-*p*-nitro-phenol $C_6H_2Br_2(NO_2)(OH)$ [1:5:3:6]. [142°] (Lellmann a. Grothmann, *B.* 17, 2731).

Formation.—1. By brominating *p*-nitrophenol or its sulphonic acid (Brunck, *Z.* 1867, 204; Post a. Brackebusch, *A.* 205, 94).—2. By nitrating tri-bromo-phenol dissolved in HOAc (Armstrong a. Harrow, *loc. cit.*).—3. In small quantity by heating the isomeride [117°] with Br (Ling, *C. J.* 51, 147).

Properties.—Prisms, sl. sol. water, v. sol. alcohol and ether.

Salt.—BaA'_2 10 aq: yellow needles, effervescing to a red powder.—BaA'_2 3½aq.—AgA′.

Methyl ether MeA′: [123°] (Körner, *G.* 4, 390). From di-bromo-anisic acid and HNO_3, the CO_2H being displaced by NO_2 (Balbiano, *G.* 14, 9). Pyramidal needles; converted by NH_3 into di-bromo-*p*-nitro-aniline [203°].

Ethyl ether [108°]. Long quadratic columns (Staedel, *A.* 217, 67).

Benzyl ether $C_6H_2Br_2(NO_2)(OC_7H_7)$. [94°]. Nearly colourless needles (from alcohol). Insol. water, sl. sol. alcohol, ether, benzene, chloroform, and glacial acetic acid (R. a. H.). Reduced by Sn and HCl to di-bromo-*p*-amido-phenol (*q. v.*) and benzyl chloride.

Tri-bromo-nitro-phenol $C_6HBr_3(NO_2).OH$ [6:4:2:3:1]. [85°] (L.); [89°] (D.). Formed by heating *m*-nitro-phenol with Br (3 mols.) at 100° (Lindner, *B.* 18, 614). Colourless crystalline powder; v. sol. alcohol, ether, and benzene, v. sl. sol. hot water.

Salts.—$A'NH_4$: sparingly soluble microscopic needles.—A′K aq: v. sol. water.—A'_2Ba 8aq: sparingly soluble orange-yellow crystals.—A'_2Ba aq.—A'_2Mgx: easily soluble red plates.

o-Nitro-benzoyl derivative $C_6HBr_3(NO_2)O.CO.C_6H_4(NO_2)$: [129° cor.]; very small colourless needles.

m-Nitro-benzoyl derivative $C_6HBr_3(NO_2)O.CO.C_6H_4(NO_2)$: [154° cor.]; glistening colourless needles; S. (90 p.c. alcohol) ·253 at 14° (Daccomo, *B.* 18, 1167).

Ethyl ether EtA′: [79°]; prisms.

BROMO-NITRO-PHENOL SULPHONIC ACID $C_6H_4BrNSO_6$ *i.e.* $C_6H_2Br(NO_2)(OH)SO_3H$ [1:3:6:5]. Formed, together with di-bromo-nitro-phenol, by brominating (1, 4, 3)-nitro-phenol sulphonic acid (Post a. Brackebusch, *A.* 205, 92).—CaA'_2 3aq. —BaA'_2 3aq.—$C_6H_2BrNSO_6(PbOH)_2$ 2½aq.

Bromo-phenol sulphonic acids have been obtained by Armstrong (*C. J.* 25, 857; *B.* 7, 404, 924) and Post (*B.* 7, 169) by the action of nitric acid on various brominated phenol sulphonic acids, and by the action of bromine on (1, 2, 5)-nitro-phenol sulphonic acid.

BROMO-NITRO-DIPHENYL $C_{12}H_8BrNO_2$ *i.e.* [4:1] $C_6H_4Br.C_6H_4(NO_2)$ [1:4]. [173°]. (above 360°). Formed by heating diphenyl (1 pt.) with conc. HNO_3 (1 pt.), or from amido-nitro-diphenyl by the diazo- reaction (Schultz, *A.* 174, 218). Long white needles (from toluene). CrO_3 gives *p*-bromo-benzoic acid and a little *p*-nitro-benzoic acid.

Bromo-nitro-diphenyl $C_{12}H_8BrNO_2$ *i.e.* [4:1] $C_6H_4Br.C_6H_4(NO_2)$ [1:2]. [65°]. (c. 360°). Formed together with the preceding. Monoclinic columns. CrO_3 gives *p*-bromo-benzoic acid (Schultz, *A.* 207, 348).

Di-bromo-nitro-diphenyl $C_6H_4Br.C_6H_3Br(NO_2)$. [127°]. Formed by nitration of di-bromo-diphenyl in acetic acid solution (Lellmann, *B.* 15, 2837). Yellowish crystals; v. sol. alcohol, benzene, and acetic acid.

Di-bromo-di-nitro-diphenyl $C_{12}H_6Br_2(NO_2)_2$. From *pp*-di-bromo-diphenyl and fuming HNO_3 (Fittig, *A.* 132, 206; S.). Hair-like crystals (from benzene). Sn and HCl give di-bromo-di-amido-diphenyl [89°].

Di-bromo-tri-nitro-diphenyl $C_6H_3Br(NO_2).C_6H_2Br(NO_2)_2$. [177°]. Formed by nitration of di-bromo-diphenyl with cold fuming HNO_3 (1·55) (Lellmann, *B.* 15, 2838). Small colourless needles. Sol. benzene, sl. sol. alcohol.

BROMO-NITRO-PHENYL ACETIC ACID $C_6H_3Br(NO_2)CH_2CO_2H$ [1:2:4]. [114°]. Formed by nitration of a mixture of *o*- and *p*-bromo-phenyl-acetic acids (Bedson, *C. J.* 37, 97). Flat greenish-yellow needles. Sol. hot, insol. cold water. V. sol. alcohol and ether. $K_2Cr_2O_7$ and H_2SO_4 give $C_6H_3Br(NO_2)CO_2H$ [199°].

Salts.—BaA'_2 aq. Its aqueous solution gives white pps. with $AgNO_3$, $Pb(OAc)_2$, and a blue pp. with $Cu(OAc)_2$.

Methyl ether. MeA′. [41°]. Needles.

Ethyl ether. Oil.

(α)-Bromo-nitro-phenyl-acetic acid $C_6H_3Br(NO_2)CH_2.CO_2H$. [169°]. Formed by nitration of mixture of *o*- and *p*-bromo-phenyl-acetic acids (Bedson). Yellowish-white, branching needles. V. sol. alcohol and ether, insol. cold, sol. hot water.

Salt.—BaA'_2 4aq. Its aqueous solution gives white pps. with $AgNO_3$ and $Pb(OAc)_2$, but a green pp. with $Cu(OAc)_2$.

Methyl ether [68°]. Flat needles.

Ethyl ether. Yellowish needles.

(β)-Bromo-nitro-phenyl-acetic acid $C_6H_3Br(NO_2)CH_2.CO_2H$. [162°]. Formed together with the two preceding (Bedson). Small yellow prisms.

BROMO-DI-NITRO-DI-PHENYL-AMINE $C_{12}H_8BrN_3O_4$ *i.e.* $C_6H_2Br(NO_2)_2.NH.C_6H_5$. *Phenyl-bromo-nitro-phenyl-amine.* [120°]. Formed by warming bromo-di-nitro-benzene [100°] with aniline (Austen, *B.* 9, 920). Orange hair-like needles (from alcohol).

Bromo-di-nitro-di-phenyl-amine $C_6H_4Br.NH.C_6H_3(NO_2)_2$. *Bromo-phenyl-di-nitro-phenyl-amine.* [153°]. From (1, 2, 4)-bromo-di nitro-benzene and di-*p*-bromo-di-phenyl-urea at 170°. Yellow needles (from ether) (Willgerodt, *B.* 11, 602).

Bromo-tri-nitro-di-phenyl-amine $C_6H_2Br(NO_2)_2.NH.C_6H_4NO_2$. [158°]. From bromo-di-nitro-di-phenyl-amine [120°] and HNO_3 (A.).

Di-bromo-di-nitro-di-phenyl-amine $C_{12}H_7Br_2(NO_2)_2N$. [196°]. Formed by bromination of di-nitro-di-phenyl-amine (Leymann, *B.* 15, 1236).

Di-bromo-tetra-nitro-di-phenyl-amine $C_6H_2Br(NO_2)_2.NH.C_6H_2Br(NO_2)_2$. [235°–242°].

From $NMe(C_6H_2Br_3)(C_6H_4Br)$ and HNO_3 (Gnehm, *B.* 8, 929). Laminæ (from HOAc).

Tri-bromo-di-nitro-di-phenyl-amine $C_{12}H_6Br_3(NO_2)_2N$. [210°]. Formed by nitrating tetra-bromo-di-phenyl-amine $(C_6H_3Br_2)_2NH$ (Gnehm a. Wyss, *B.* 10, 1323).

BROMO-NITRO-PHENYL BENZYL OXIDE *v.* BROMO-NITRO-PHENOL, *Benzyl ether.*

DI-BROMO-NITRO-PHENYL-CARBAMIC ACID. *Methyl ether* [1:3:4] $C_6H_2Br_2(NO_2).NH.CO_2Me$. [152°]. From methyl-(1,3,4)-di-bromo-phenyl-carbamate and HNO_3 (Hentschel, *J. pr.* [2] 34, 425). Prisms (from alcohol). NH_3 forms (1,3,4)-di-bromo-aniline.

BROMO-NITRO-*m*-PHENYLENE-DIAMINE $C_6H_6BrN_3O_2$ *i.e.* $C_6H_2Br(NO_2)(NH_2)_2$ [1:2:3:5]. From tri-bromo-nitro-benzene and alcoholic NH_3 for some days at 175° (Körner, *G.* 4). Orange needles; decomposes at 163°. Converted into *p*-bromo-benzene by the diazo- reaction.

Bromo-nitro-*p*-phenylene-diamine $C_6H_2Br(NO_2)(NH_2)_2$ [1:4:2:5]. [156°]. From tri-bromo-nitro-benzene [94°] and alcoholic NH_3 at 110° (Körner, *G.* 4). Pyramidal needles. Converted by diazo- reaction into *p*-bromo-benzene.

BROMO-NITRO-PHENYL-ETHANE *v.* BROMO-NITRO-ETHYL-BENZENE.

Di-bromo-di-nitro-*s*-di-phenyl-ethane $C_6H_4(NO_2).CHBr.CHBr.C_6H_4.NO_2$. [above 300°]. *Di-bromide of di-p-nitro-stilbene.* Split up by heat into 2HBr and di-nitro-tolane (Elbs a. Bauer, *J. pr.* [2] 31, 315).

Di-bromo-di-nitro-*s*-di-phenyl-ethane $C_{14}H_{10}Br_2(NO_2)_2$. *Di-bromo-di-nitro-di-benzyl.* [205°]. Formed by nitrating di-*p*-bromo-dibenzyl (Fittig a. Stelling, *A.* 137, 260). Sword-shaped crystals (from benzene).

BROMO-NITRO-PHENYL ETHYL OXIDE *v.* *Ethyl*-BROMO-NITRO-PHENOL.

αα-DI-BROMO-αm-DI-NITRO-ω-PHENYL-METHYL-CARBINOL.

Ethyl ether $CBr_2(NO_2).CH(C_6H_4NO_2).OEt$. [99°].—1. From the compound of alcohol with *αm*-di-nitro-cinnamic ether (*q.v.*) by simultaneous treatment with aqueous NaOH and Br (Friedländer a. Lazarus, *A.* 229, 237).—2. From *ω-m*-di-nitro-styrene, alcohol, aqueous NaOH and Br. White plates (from dilute alcohol). Insoluble in aqueous NaOH.

Methyl ether $CBr_2(NO_2).CH(C_6H_4NO_2)OMe$. [146°]. Formed in a similar way from the compound of methyl alcohol with the same body, or from *ω-m*-di-nitro-styrene, methyl alcohol, Br_2 and aqueous NaOH. White plates.

BROMO-NITRO-PHENYL-METHYL-KETONE *v.* BROMO-NITRO-ACETOPHENONE.

***p*-BROMO-*o*-NITRO-β-PHENYL-PROPIONIC ACID** $C_6H_3(Br)(NO_2)C_2H_4.CO_2H$ [4:2:1]. *Bromo-nitro-hydrocinnamic acid.* [112°]. Prepared by the action of HBr on the diazo-compound from *p*-amido-*o*-nitro-hydrocinnamic acid. Formed together with the (4,3,1)-isomeride by nitration of *p*-bromo-hydrocinnamic acid. Flat feathery crystals. By reduction with tin and HCl it gives *p*-bromo-hydrocarbostyril (Gabriel a. Zimmermann, *B.* 13, 1682).

***p*-Bromo-*m*-nitro-β-phenyl-propionic acid** $C_6H_3(Br)(NO_2).C_2H_4.CO_2H$ [4:3:1]. [90°-95°]. Long glistening needles. Prepared as above. On reduction with tin and HCl it gives *p*-bromo-*m*-amido-hydrocinnamic acid (Gabriel a. Zimmermann, *B.* 13, 1683).

β-Bromo-*o*-nitro-β-phenyl-propionic acid $C_6H_4(NO_2).CHBr.CH_2.CO_2H$. [140°]. From *o*-nitro-cinnamic acid, HOAc, and HBr at 100° (Einhorn, *B.* 16, 2208). Monoclinic crystals; v. sol. ordinary solvents, sl. sol. benzene.

Reactions.—1. *Boiling water* forms indoxyl. 2. NaOHAq forms nitro-cinnamic acid.—3. Cold Na_2CO_3Aq forms the lactone of *o*-nitro-β-oxy-phenyl-propionic acid.—4. Hot Na_2CO_3Aq gives nitro-cinnamic acid, nitro-oxy-phenyl-propionic acid, and *o*-nitro-styrene.

β-Bromo-*m*-nitro-β-phenyl-propionic acid $C_6H_4(NO_2).CHBr.CH_2.CO_2H$. [96°]. Prepared by heating an acetic acid solution of *m*-nitro-cinnamic acid with HBr at 100°. V. sol. alcohol, sl. sol. toluene, insol. petroleum-ether.

Reactions.—1. By boiling with water it chiefly gives *m*-nitro-styrene.—2. An excess of alkali converts it back into *m*-nitro-cinnamic acid.—3. By adding the powdered acid to an aqueous solution of ½ mol. of Na_2CO_3, it yields 30 p.c. of *m*-nitro-styrene, 20 p.c. of *m*-nitro-cinnamic acid, and 10 p.c. of *m*-nitro-β-oxy-β-phenyl-propionic acid. If the powdered acid is added to a cold solution of Na_2CO_3 the β-lactone is formed (Prausnitz, *B.* 17, 595).

β-Bromo-*p*-nitro-phenyl-propionic acid $C_6H_4(NO_2).CHBr.CH_2.CO_2H$. [172°]. Prepared by heating *p*-nitro-cinnamic ether with HBr at 100°. Prisms; sol. hot alcohol, sl. sol. water and benzene.

Reactions.—1. Long boiling with dilute H_2SO_4 (25 p.c.) reconverts it into *p*-nitro-cinnamic acid.—2. Heated with *water* it yields *p*-nitro-β-oxy-phenyl-propionic acid (72 p.c.) and *p*-nitro-styrene (28 p. c.).—3. Cold aqueous KOH gives *p*-nitro-oxy-phenyl-propionic acid and its lactone. Alcoholic KOH yields almost entirely *p*-nitro-cinnamic acid.—4. Aqueous NH_3 yields the lactone which by excess of NH_3 is converted into the corresponding amido- acid.

Ethyl ether A'Et. [81°]; colourless plates (Basler, *B.* 16, 3001).

Di-bromo-*o*-nitro-phenyl-propionic acid $C_6H_4(NO_2)CHBr.CHBr.CO_2H$. *Dibromide of o-nitro-cinnamic acid.* [c. 180°]. From Br and *o*-nitro-cinnamic acid (Baeyer, *B.* 13, 2257). Needles or plates; sol. hot water. NaOHAq gives *o*-nitro-phenyl-propiolic acid. Zinc-dust and NaOH gives indol.

Methyl ether MeA'. [99°].

Ethyl ether EtA'. [71° uncor.] (M.) From *o*-nitro-cinnamic ether and Br (Müller, *A.* 212, 130). Alcoholic KOH converts it into *o*-nitro-phenyl-propiolic acid. Heated with water at 120° it gives *o*-nitro-cinnamic acid.

Di-bromo-*p*-nitro-phenyl-propionic acid $C_6H_4(NO_2)CHBr.CHBr.CO_2H$. [218°]. From *p*-nitro-cinnamic acid and Br (Drewson, *A.* 212, 151). Rhombic prisms (from glacial HOAc). M. sol. water or glacial HOAc, v. sol. alcohol or ether, sl. sol. benzene, v. sl. sol. benzoline. Aqueous NaOH forms *p*-nitro-cinnamic and *p*-nitro-phenyl-propiolic acids.—CaA'_2.

Ethyl ether EtA'. [111°]. From *p*-nitro-cinnamic ether and Br in CS_2 (C. L. Müller, *A.* 212, 129). Columns (from CS_2); v. sol. hot alcohol, ether, or benzoline. Alcoholic KOH converts it into a mixture of two isomeric bromo-*p*-

nitro-cinnamic ethers, and *p*-nitro-phenyl-propiolic acid. Heated with water at 120° it gives *p*-nitro-cinnamic acid.

BROMO-NITRO-PHTHALIC ACID $C_6H_2Br(NO_2)(CO_2H)_2$ [1:4:2:3]. From di-bromo-naphthalene [82°] and HNO_3.—Na_2A'' (Guareschi, *A.* 222, 277).

α-BROMO-ω-NITRO-PROPANE $CH_3.CH_2.CHBr(NO_2)$. (c. 160°). Formed together with di-bromo-nitro-propane by the action of potash and Br on nitro-propane (V. Meyer a. Tscherniak, *A.* 180, 116). Oil, sol. potash.

α-Bromo-α-nitro-propane $CH_3.CBr(NO_2).CH_3$. (150°). From $CH_3.CH(NO_2).CH_3$. Insol. potash.

Di-bromo-nitro-propane $CH_3.CH_2.CBr_2(NO_2)$. (184°-186°). From bromo-nitro-propane, Br, and potash. An oil, insol. potash.

TRI-BROMO DI-NITRO-PROPIONIC ACID $C_3HBr_3N_2O_6$ *i.e.* $CBr_3.C(NO_2)_2.CO_2H$. From tri-bromo-phloroglucin and conc. HNO_3 (Benedikt, *A.* 184, 255). Silky scales, insol. cold water, v. e. sol. alcohol and ether; decomposed by boiling water.

BROMO - NITRO - PROPYL - BENZENE *v.* BROMO-NITRO-CUMENE.

BROMO-NITRO-PROPYL-PHENOL *v.* BROMO-CUMENOL.

DI-BROMO-DI-NITRO-PYRROL

$C_4HBr_2N_3O_4$ *i.e.* $\begin{matrix} CBr:C(NO_2) \\ | \\ CBr:C(NO_2) \end{matrix}\!\!>\!NH$. [169°].

Formed by dissolving di-bromo-nitro-pyrryl methyl ketone [206°] in a mixture of fuming HNO_3 and conc. H_2SO_4 at −18°, and precipitating in water. Silky leaflets (containing aq). At the ordinary temperature it is converted into di-bromo-maleïmide (Ciamician a. Silber, *B.* 20, 699; *G.* 17, 262).

DI-BROMO-NITRO-PYRRYL METHYL KETONE $\begin{matrix} CBr:C(NO_2) \\ | \\ CBr:C-CO.CH_3 \end{matrix}\!\!>\!NH$. [206°]. Long needles.

Formed by the action of cold nitric acid upon di-bromo-pyrrylene-di-methyl-di-ketone $\begin{matrix} CBr:C-CO.CH_3 \\ | \\ CBr:C-CO.CH_3 \end{matrix}\!\!>\!NH$, [171°], which is formed by passing bromine-vapour into pyrrylene di-methyl di-ketone (Ciamician a. Silber, *B.* 20, 699).

Di-bromo-nitro-pyrryl methyl ketone $\begin{matrix} CBr:CBr \\ | \\ C(NO_2):C-CO.CH_3 \end{matrix}\!\!>\!NH$. [175°]. From nitro-pyrryl methyl ketone [197°] and Br. Needles.

BROMO-NITRO-QUINOLINE $C_9H_5N(Br)(NO_2)$ [133°]. Formed by nitration of bromo-quinoline. Long glistening needles. Volatile undecomposed. Sol. alcohol and ether, sl. sol. water. Weak base. $-B'_2H_2Cl_2PtCl_4$: short orange-yellow prisms (La Coste, *B.* 15, 1918).

DI-BROMO-NITRO-QUINONE $C_6HBr_2(NO_2)O_2$ [6:2:3:4:1]. [246°]. Yellow plates; v. sl. sol. hot water and cold alcohol. Formed by the action of a mixture of HNO_3 and H_2SO_4 upon the propionyl derivative of tri-bromo-phenol (Guareschi a. Daccomo, *B.* 18, 1174).

BROMO-NITRO-RESORCIN *Ethyl ether* $C_6H_2Br(NO_2)(OH)(OEt)$. [114°]. From ethyl (1, 2, 4)-nitro-resorcin and Br (Weselsky, *M.* 1, 898).

Di-bromo-nitro-resorcin $C_6H_3Br_2NO_4$ *i.e.* $C_6HBr_2(NO_2)(OH)_2$. [147°]. From (1, 2, 4)-nitro-resorcin [115°] in ether and Br (Weselsky, *A.* 164, 7). Golden laminæ.—$Ba(C_6H_2Br_2NO_4)_2$ 4aq.

Ethyl ether $C_6HBr_2(NO_2)(OEt)(OH)$ [1:5:3:2:6]. [69°]. From ethyl nitro-resorcin and Br (W.).

Di-bromo-nitro-resorcin $C_6HBr_2(NO_2)(OH)_2$ [1:3:5:4:6]. [117°]. From (1, 2, 6)-nitro-resorcin and Br (W.).

Bromo-di-nitro-resorcin $C_6HBr(NO_2)_2(OH)_2$. [193°]. Formed by nitrating di-bromo-nitroso-resorcin or by brominating di-nitro-resorcin (Fèvre, *Bl.* [2] 39, 590; *C. R.* 96, 790; Typke, *B.* 16, 555). Orange needles; sl. sol. boiling alcohol.—K_2A'' ½aq: red needles.—Na_2A''2aq.—BaA'' 3aq.—$(NH_4)_2A''$aq.

Acetyl derivative: [135°]; prisms.

BROMO-NITRO-SALICYLIC ACID *v.* BROMO-NITRO-OXY-BENZOIC ACID.

DI-BROMO-NITROSO-RESORCIN $C_6HBr_2(NO)(OH)_2$. From nitroso-resorcin and Br (Fèvre, *Bl.* [2] 39, 591). Yellowish needles (containing 2aq) which turn brown at 138° and decompose at 150°; insol. benzene, sl. sol. cold water, v. e. sol. alcohol.

BROMO-NITROSO-THYMOL $C_6HMePrBr(NO)(OH)$. [c. 135°]. From nitroso-thymene and Br (Mazzara a. Descalzo, *G.* 16, 196).

BROMO-NITRO-STYRENE $Ph.CBr:CHNO_2$. [68°]. From di-bromo-nitro-phenyl-ethane $PhCBrH.CHBrNO_2$ and aqueous NaOH (Priebs, *A.* 225, 343). Golden needles or plates (from light petroleum). Smells something like hay; when freshly ppd. from alcoholic solution by water it is soluble in alkalis, hence its constitution is as above, rather than $Ph.CH:CBr(NO_2)$.

DI-BROMO-DI-NITRO-THIOPHENE $C_4SBr_2(NO_2)_2$. [134°]. Light-yellow crystals. V. sol. hot alcohol. Formed by nitration of di- or tri-bromo-thiophene (Kreis, *B.* 17, 2074; Rosenberg, *B.* 18, 3029).

TRI-BROMO-NITRO-THIOPHENE $C_4SBr_3(NO_2)$. [106°]. Formed by nitration of tri-bromo-thiophene. Felted yellow needles. V. sol. ether, sl. sol. alcohol (Rosenberg, *B.* 18, 3028).

BROMO-NITRO-THYMOL $C_6HMePrBr(NO_2)(OH)$. [101°]. From bromo-nitroso-thymol and K_3FeCy_6 (Mazzara, *G.* 16, 196).

BROMO-NITRO-TOLUENE $C_6H_3Me(NO_2)Br$ [1:2:3]. Oil. From bromo-nitro-*m*-toluidine by nitrous gas and alcohol (Nevile a. Winther, *C. J.* 37, 630).

Bromo-nitro-toluene $C_6H_3Me(NO_2)Br$ [1:3:4]. [32°]. (256°). S.G. $\frac{18}{}$ 1·631. From the corresponding nitro-toluidine by the diazo-perbromide reaction (Nevile a. Winther, *C. J.* 37, 442). Formed also by nitrating *p*-bromo-toluene (Wroblewsky, *A.* 168, 176) and by treating *m*-nitro-toluene with Br and $FeBr_2$ at 70° (Scheufelen, *A.* 231, 180).

Bromo-nitro-toluene $C_6H_3Me(NO_2)Br$ [1:2:4]. [45°]. (257°). From the corresponding nitro-toluidine [78°] by the diazo-perbromide reaction (Beilstein a. Kuhlberg, *A.* 158, 340; Nevile a. Winther, *C. J.* 37, 441). Formed also, together with the preceding, by nitrating *p*-bromo-toluene (W.). Large monoclinic tables.

Bromo - nitro - toluene $C_6H_3Me(NO_2)Br$ [1:2 or 6:3]. [55°]. (267°). Formed by nitrating *m*-bromo-toluene (W.; Grete, *A.* 177, 246).

Trimetric crystals; on reduction it gives bromo-o-toluidine.

Bromo-nitro-toluene $C_6H_3Me(NO_2)Br$ [1:4:2]. [77°]. From $C_6H_2(CH_3)Br(NO_2)(NH_2)$ [1:2:4:5] (Nevile a. Winther, *C. J.* 39, 85). From *p*-nitro-toluene, $FeBr_2$, and bromine (Scheufelen, *A.* 231, 171). Also from diazo-nitro-toluene piperidide $C_6H_3Me(NO_2).N_2.NC_5H_{10}$ and boiling HBrAq (Wallach, *A.* 235, 248). Needles.

Bromo-nitro-toluene $C_6H_3Me(NO_2)Br$ [1:3:6]. [78°]. From *m*-nitro-toluene, $FeBr_2$, and bromine (Scheufelen, *A.* 231, 179). From (3, 1, 6)-nitro-*o*-toluidine (N. a. W.).

Bromo-nitro-toluene $C_6H_3Me(NO_2)Br$ [1:3:5]. [81°]. (N. a. W.); [86°] (W.); (270°). Formed (*a*) from bromo-nitro-*p*-toluidine [65°], (*b*) from nitro-(5, 1, 2)-bromo-*o*-toluidine [143°], or (*c*) from bromo-nitro-*o*-toluidine [181°] by the usual methods (Nevile a. Winther, *C. J.* 37, 431; Wroblewsky, *A.* 192, 203). Hence it can be prepared from a mixture of acetyl *o*- and *p*-toluidines by successive bromination, nitration, saponification, and diazotisation.

Bromo-di-nitro-toluene $C_6H_2Me(NO_2)_2Br$. [104°]. From *m*-bromo-toluene and fuming HNO_3 (Grete, *A.* 177, 258).

Di-bromo-nitro-toluene $C_6H_2Me(NO_2)Br_2$ [1:4 or 6:2:3]. [c. 57°]. From $C_6H_3(CH_3)Br_2$ [28°] by nitration (Nevile a. Winther, *C. J.* 37, 434).

Di-bromo-nitro-toluene $C_6H_2Me(NO_2)Br_2$ [1:4:2:6]. [58°]. From $C_6H(CH_3)(NH_2)(NO_2)Br_2$ [124°–130°] by ethyl nitrite (Nevile a. Winther, *C. J.* 37, 445). Also from (2,4,1)-bromo-nitro-toluene, $FeBr_2$, and Br (Scheufelen, *A.* 231, 178).

Di-bromo-nitro-toluene $C_6H_2Me(NO_2)Br_2$ [1:5:3:4]. [63°]. From bromo-nitro-toluidine, $C_6H_2(CH_3)(NO_2)(NH_2)Br$ [1:5:4:3] by diazo-perbromide reaction (Nevile a. Winther, *C. J.* 37, 447). Colourless plates (from alcohol).

Di-bromo-nitro-toluene $C_6H_2Me(NO_2)Br_2$ [1:3:2:5]. [70°]. From bromo-nitro-*o*-toluidine, [143°], by diazo-perbromide reaction (Nevile a. Winther, *C. J.* 37, 448).

Di-bromo-nitro-toluene $C_6H_2MeBr_2(NO_2)$ [1:4:6:2?]. [80°]. By nitrating di-bromo-toluene from di-bromo-*m*-toluidine, [75°] (Nevile a. Winther, *C. J.* 37, 441).

Di-bromo-nitro-toluene $C_6H_2Me(NO_2)Br_2$ [1:6:3:4]. [87°]. Formed by nitrating the corresponding di-bromo-toluene. Converted by reduction and diazo-reaction into (2, 4, 5, 1)-tri-bromo-toluene [113°] (Nevile a. Winther, *C. J.* 39, 83).

Di-bromo-nitro-toluene $C_6H_2Me(NO_2)Br_2$ [1:4:2:5]. [88°]. From $C_6H_2(CH_3)(NO_2)(NH_2)Br$, [181°] by the diazo-perbromide reaction. Formed also by nitrating $C_6H_3(CH_3)Br_2$ [1:2:5]. Converted by reduction and diazotisation into (2, 4, 5, 1)-tri-bromo-toluene [113°] (Nevile a. Winther, *C. J.* 37, 445; 39, 83).

Di-bromo-nitro-toluene $C_6H_2Me(NO_2)Br_2$ [1:3:5:6]. [106°]. From bromo-nitro-*o*-toluidine, [181°], by exchange of NH_2 for Br (Nevile a. Winther, *C. J.* 37, 433).

ω-Di-bromo-nitro-toluene $C_6H_5.CBr_2(NO_2)$. *Phenyl-di-bromo-nitro-methane.* Colourless oil. Formed by the action of bromine upon an aqueous solution of the di-sodium salt of nitro-benzylidene-phthalide

$$C_6H_4\left<\begin{matrix}C(ONa){=}CNa(NO_2).C_6H_5\\ \quad\quad\quad > O\\ CO\end{matrix}\right.$$

Volatile with steam (Gabriel a. Koppe, *B.* 19, 1145).

Di-bromo-di-nitro-toluene $C_6HMe(NO_2)_2Br_2$. [158°]. Formed by nitrating $C_6H_3(CH_3)Br_2$, [39°] (Nevile a. Winther, *C. J.* 37, 437).

Di-bromo-di-nitro-toluene $C_6HMe(NO_2)_2Br_2$ [105°]. Formed at the same time as the preceding (N. a. W.).

Di-bromo di-nitro-toluene $C_6HMe(NO_2)_2Br_2$ [1:?:?:2:6]. [161°]. By nitration of (2, 6, 1)-di-bromo-toluene (N. a. W.).

Tri-bromo-nitro-toluene $C_6HMe(NO_2)Br_3$ [1:4:2:5:6]. [106°]. From di-bromo-nitro-*m*-toluidine, [125°–130°], by the diazo-perbromide reaction. White needles (Nevile a. Winther, *C. J.* 39, 85).

Tri-bromo-nitro-toluene $C_6HMe(NO_2)Br_3$. [107°]. [1:*x*:2:3:4]. Formed by nitrating tri-bromo-toluene, [44°] (N. a. W.).

Tri-bromo-nitro-toluene $C_6HMe(NO_2)Br_3$ [1:3:2:4:6]. [215°]. Formed by nitrating tri-bromo toluene [70°] (Wroblewsky, *A.* 168, 195).

Tri-bromo-di-nitro-toluene $C_6Me(NO_2)_2Br_3$ [1:?:?:2:3:4]. [217°–220°]. Formed by nitrating tri-bromo-toluene [44°] (Nevile a. Winther, *B.* 13, 975).

Tetra-bromo-nitro-toluene $C_6Me(NO_2)Br_4$ [1:4:2:3:5:6]. [213°] (N. a. W.); [227°] (S.). Formed by nitration of $C_6H(CH_3)Br_4$, [117°] (Nevile a. Winther, *C. J.* 37, 450). From (2,4,1)-bromo-nitro-toluene, bromine, and $FeBr_2$ (Scheufelen, *A.* 231, 179).

Tetra-bromo-nitro-toluene $C_6Me(NO_2)Br_4$ [1:2:3:4:5:6]. [212°]. From tetra-bromo-toluene, [111°].

Tetra-bromo-nitro-toluene $C_6Me(NO_2)Br_4$ [1:5:2:3:4:6]. [216°]. By nitration of tetra-bromo toluene, [108°].

BROMO-NITRO-TOLUENE SULPHONIC ACIDS $C_6H_2MeBr(NO_2)SO_3H$. The six following acids of this constitution have been described.

I. Formed by nitrating *o*-bromo-toluene sulphonic acid (Müller, *A.* 169, 42; Pagel, *A.* 176, 299). Deliquescent. — PbA'_2 2aq. — NaA'aq. — KA'. — BaA'_2 2aq.

II. By the action of fuming HNO_3 on (2,1,4)-bromo-toluene sulphonic acid or on (2,1,4)-*o*-toluidine sulphonic acid: in the latter case the resulting diazo-nitro-toluene sulphonic acid is boiled with HBrAq (Hayduck, *A.* 172, 219; 174, 347). Minute needles; may be reduced to (1,3,4)-*m*-toluidine sulphonic acid. — BaA'_2 3aq.

Chloride $C_6H_2MeBr(NO_2)SO_2Cl$. [220°].

Amide $C_6H_2MeBr(NO_2)(SO_2NH_2)$. Does not melt below 200°.

III. From *m*-bromo-toluene sulphonic acid and HNO_3 (Wroblewsky, *A.* 168, 169). — CaA'_2 4½aq. — BaA'_2 3½aq. — PbA'_2 3aq.

IV. Formed by nitrating (3, 1, 2 or 6)-*m*-bromo-toluene sulphonic acid (Weckwarth, *A.* 172, 200). — NaA'. — CaA'_2 3aq. — BaA'_2 3½aq.

V. Formed by nitrating (4,1,2)-*p*-bromo-toluene sulphonic acid (Hässelbarth, *A.* 169, 22). Deliquescent laminæ. — AgA'. — BaA'_2 2aq. — CaA'_2 6aq. — PbA'_2 3aq. — SrA'_2 7aq.

VI. Formed by nitrating (4,1,3)-*p*-bromo-toluene sulphonic acid (H.). Deliquescent needles.—BaA'_2aq.—$PbA'_2 2\frac{1}{2}$aq.—$SrA'_2$5aq.

Di-bromo-nitro-toluene-di-sulphonic acid $C_6HBr_2(NO_2)Me.SO_3H$. From *p*-bromo-toluene di-sulphonic acid and boiling fuming HNO_3 (Kornatzki, *A.* 221, 197).—KA′aq.—$BaA'_2 3\frac{1}{2}$aq.

BROMO-NITRO-*m*-TOLUIC ACID $C_8H_6BrNO_4$ *i.e.* $C_6H_2MeBr(NO_2)(CO_2H)$. [176°]. From bromo-*m*-toluic acid and HNO_3 (Fittig, *A.* 147, 34).—CaA'_2 3aq.—BaA'_2 3aq.

Bromo-nitro-*p*-toluic acid $C_6H_2MeBr(NO_2)(CO_2H)$ [4:2:*x*:1]. [200°]. S. ·1 at 15°. Formed by boiling bromo-cymene (from thymol) with HNO_3 (S.G. 1·3). Laminæ. —$BaA'_2$4aq (Fileti a. Crosa, *G.* 16, 297).

Bromo-nitro-*p*-toluic acid $C_6H_2MeBr(NO_2)(CO_2H)$ [4:3:*x*:1]. [170°–180°]. From bromo-*p*-toluic acid and fuming HNO_3 (Landolph, *B.* 5, 268). Needles (from water).— BaA'_2aq.

BROMO-NITRO-*o*-TOLUIDINE $C_6H_2Me(NH_2)(NO_2)Br$ [1:2:3:5]. [139°] (W.); [143°] (N. a. W.). Formed by nitrating bromo-acetyl-*o*-toluidine, $C_6H_3Me(NHAc)Br$ [1:2:5], and removing acetyl (Wroblewsky, *A.* 192, 206; Nevile a. Winther, *C. J.* 37, 431). Gives, by nitrous gas and alcohol, $C_6H_3Me(NO_2)Br$, [81°] whence $C_6H_3Me(NH_2)Br$, [35°].

Bromo-nitro-*o*-toluidine $C_6H_2Me(NH_2)(NO_2)Br$ [1:2:5:3]. [181° cor.]. By brominating $C_6H_3Me(NH_2)(NO_2)$ [1:2:3], [128°] (N. a. W.). Converted by nitrous gas and alcohol into $C_6H_3Me(NO_2)Br$, [81°] whence $C_6H_3Me(NH_2)Br$ [36°].

Bromo-nitro-*m*-toluidine $C_6H_2Me(NH_2)(NO_2)Br$ [1:3:6:5]. [88°]. Formed by nitrating bromo-acetyl-*m*-toluidine, and then removing acetyl by H_2SO_4 (2 vols.) and water (1 vol.) (Nevile a. Winther, *C. J.* 37, 630).

Bromo-nitro-*m*-toluidine $C_6H_2Me(NH_2)(NO_2)Br$ [1:3:2:6]. [183°]. Is formed in small quantity in the preparation of its isomeride [181°].

Bromo-nitro-*m*-toluidine $C_6H_2Me(NH_2)(NO_2)Br$ [1:5:4:2] [181°]. From the acetyl derivative by saponification.

Acetyl derivative [110°–121°]. Formed by nitration of bromo-acetyl-*m*-toluidine (Nevile a. Winther, *C. J.* 37, 441).

Bromo-nitro-*p*-toluidine $C_6H_2Me(NH_2)(NO_2)Br$ [1:4:3:5]. [64·5°]. Got by saponifying its acetyl derivative. Orange needles. Converted by nitrous gas and alcohol into bromo-nitro-toluene [86°] (*cf.* Hand, *A.* 234, 157).

Acetyl derivative [211°]. From bromo-acetyl-*p*-toluidine and HNO_3. Or from acetyl-*p*-toluidine by successive nitration and bromination (N. a. W.). White needles (from alcohol or dilute acetic acid) (Wroblewsky, *A.* 192, 202).

Di-bromo-nitro-*m*-toluidine $C_6HMe(NH_2)(NO_2)Br_2$ [1:5:4:2:6]. [124°–130°]. From the acetyl derivative of bromo-nitro-*m*-toluidine [181°] by heating with H_2SO_4 (2 vols.) and water (1 vol.) and subsequent treatment with bromine (Nevile a. Winther, *C. J.* 37, 444).

BROMO-NITRO-*m*-XYLENE $C_6H_2Me_2(NO_2)Br$. (260°–265°). From bromo-*m*-xylene and cold fuming HNO_3. Liquid (Fittig, *A.* 147, 31).

Di-bromo-nitro-*o*-xylene $C_6HMe_2(NO_2)Br_2$ [1:2:3:4:5]. [141°]. Obtained by nitration of di-bromo-*o*-xylene $C_6H_2(CH_3)_2Br_2$ [1:2:4:5] with cold fuming HNO_3. Colourless needles (from alcohol) (Töhl, *B.* 18, 2561).

Di-bromo-nitro-*m*-xylene $C_6HMe_2(NO_2)Br_2$. [108°]. From di-bromo-*m*-xylene and HNO_3. Needles (F.).

Di-bromo-nitro-*p*-xylene $C_6HMe_2(NO_2)Br_2$. [112°]. From di-bromo-*p*-xylene and fuming HNO_3 (F.). Needles.

Di-bromo-di-nitro-*o*-xylene $C_6(CH_3)_2Br_2(NO_2)_2$ [1:2:4:5:3:6]. [c. 250°]. Small needles. Nearly insol. cold alcohol. Formed by nitration of di-bromo-*o*-xylene $C_6H_2(CH_3)_2Br_2$ [1:2:4:5] (Töhl, *B.* 18, 2561).

BROMO-NITRO-XYLENE SULPHONIC ACID $C_6HMe_2Br(NO_2)(SO_3H)$ [1:3:6:*x*:4]. From nitro-*m*-xylidine sulphonic acid by diazo- reaction (Sartig, *A.* 230, 341; *B.* 18, 2190). Rhombic plates, v. sol. water and alcohol.—$BaA'_2 3\frac{1}{2}$aq.—KA′aq.

BROMO-NONYLIC ACID *v.* BROMO-ENNOIC ACID.

DI-BROMO-OCTADECANE $C_{18}H_{36}Br_2$. *Octadecylene bromide.* [24°]. Silvery plates. Sl. sol. alcohol. Formed by the addition of Br (1 mol.) to octadecylene (Krafft, *B.* 17, 1373).

BROMO-OCTANE *v.* OCTYL BROMIDE.

Di-bromo-octane $C_8H_{16}Br_2$. *Octylene bromide.* From Br and octylene derived from castor oil (Rubien, *A.* 142, 297) or that from paraffin (Thorpe a. Young, *Pr.* 21, 193). Non-volatile oil.

Tetra-bromo-octane $C_8H_{14}Br_4$. *Caprylidene tetra-bromide.* From bromo-octylene and Br. Oil.

BROMO-OCTONENE $C_8H_{11}Br$. (201°). From $C_8H_{14}Br_4$ (*v. supra*) and alcoholic KOH (R.).

BROMO-OCTYL-BENZENE $C_6H_4(C_8H_{17})Br$. (285°–287°). Formed by bromination of octyl-benzene. Oil (Ahrens, *B.* 19, 2719).

BROMO-OCTYLENE $C_8H_{15}Br$. (185°). From di-bromo-octane and alcoholic KOH (Rubien, *A.* 142, 297). With Br it gives an oily tri-bromo-decane.

Di-bromo-octylene $C_8H_{14}Br_2$. S.G. $\frac{16}{}$ 1·568. *Conylene bromide.* From conylene and Br (Wertheim, *A.* 123, 182).

BROMO-OCTYL-THIOPHENE $C_4SH_2(C_8H_{17})Br$. (285°–290°). Colourless oil solidifying to plates at 5°. V. sol. ether, insol. water. Formed by shaking octyl-thiophene with bromine-water (Schweinitz, *B.* 19, 644).

BROMO-OLEIC ACID $C_{18}H_{33}BrO_2$. From di-bromo-stearic acid and alcoholic KOH (Overbeck, *A.* 140, 47).

Di-bromo-oleïc acid $C_{18}H_{32}Br_2O_2$. From stearolic acid and Br (O.).

BROMO-ORCIN $C_6H_2Me(OH)_2Br$. [135°]. From orcin and bromine-water (Lamparter, *A.* 134, 258). Crystals; m. sol. hot water, v. e. sol. alcohol and ether. Solutions are ppd. by lead subacetate.

Di-bromo-orcin

Methyl derivative $C_6H(CH_3)(OMe)(OH)Br_2$. [146°]. White needles. Prepared by bromination of the mono-methyl ether of orcin (Tiemann a. Streng, *B.* 14, 2002).

Di-methyl derivative $C_6H(CH_3)(OMe)_2Br_2$. [160°]. Colourless plates. Sol. alcohol, ether, and benzene, insol. water and ligroïn. Prepared by bromination of the di-methyl ether of orcin (*B.* 14, 2001).

Tri-bromo-orcin $C_6(CH_3)Br_3(OH)_2$. [103°]. From orcin and Br (Stenhouse, *Tr.* 1848, 87; Laurent a. Gerhardt, *A. Ch.* [3] 24, 317; Lamparter, *A.* 134, 257; Hesse, *A.* 117, 311; Stenhouse a. Groves, *A.* 203, 298). Is formed by heating penta-bromo-orcin with formic acid. Needles; insol. water, sol. alcohol and ether.

Diacetyl derivative [143°]. White needles. Formed by the action of Ac_2O on penta-bromo-orcin (Claassen, *B.* 11, 1440).

Penta-bromo-orcin $C_7H_3Br_5O_2$ *i.e.* $C_6MeBr_3(OBr)_2$? [126°]. From orcin and excess of bromine-water. Triclinic crystals (from CS_2). At 160° it gives off Br_2, leaving $C_7H_4Br_4O_2$ (Stenhouse, *A.* 163, 180; Liebermann a. Dittler, *A.* 169, 252).

Bromo-β-orcin *v.* BROMO-BETORCIN.

DI-BROMO-OXAL-ETHYLINE *v.* DI-BROMO-METHYL-ETHYL-GLYOXALINE.

BROMO-OXINDOLE *v.* OXINDOLE.

BROMO-OXY-ACRYLIC ACID. *Phenyl derivative* $C_9H_7BrO_3$ *i.e.* $CHBr:C(OPh).CO_2H$. [138°]. From phenyl-oxy-mucobromic acid $CHO.CBr:C(OPh).CO_2H$ and KOH (Hill a. Stevens, *Am.* 6, 190). Needles (from water); v. e. sol. alcohol and ether.—KA'. BaA'_2 5aq. CaA'_2 5aq.—AgA'.

BROMO-OXY-AMIDO-BENZOIC ACID. *Methyl derivative* $C_8H_8BrNO_3$ *i.e.* $C_6H_2Br(OMe)(NH_2)CO_2H$. [185°]. *Bromo-amido-anisic acid.* From the corresponding nitro-acid. Needles, sl. sol. water.—CaA'_2 5½aq.—BaA'_2 2aq.—HA'HCl [186°] (Balbiano, *G.* 14, 245).

BROMO-DI-OXY-ANTHRAQUINONE $C_{14}H_7BrO_4$ *i.e.* $C_{14}H_5O_2(OH)_2Br$. *Bromo-alizarin.* From alizarin (3 pts.) and Br (2½ pts.) in CS_2 at 190° (Perkin, *C. J.* 27, 401). Tufts of orange needles; may be sublimed. KOHAq forms a blue solution, exhibiting the same absorption bands as alizarin. HNO_3 forms phthalic acid. The same bromo-alizarin, or an isomeride, is formed by treating tri-bromo-anthraquinone with KOH. It melts at 280° (Diehl, *B.* 11, 190).

Bromo-tri-oxy-anthraquinone $C_{14}H_4O_2(OH)_3Br$. *Bromo-purpurin.* [276°]. From Br and purpurin, or its carboxylic acid, or by warming di-bromo-purpurin (*v. infra*) with conc. H_2SO_4. Red needles (Plath, *B.* 10, 615, 1619; Schunck a. Roemer, *B.* 10, 554).

(*B.* 1,3,2)-**Di-bromo-oxy-anthraquinone** $C_{14}H_6Br_2O_3$ *i.e.* $C_6H_4:(C_2O_2):C_6HBr_2(OH)$. [208°]. Formed, together with di-bromo-phenol by heating tetra-bromo-phenol-phthalein with excess of H_2SO_4 at 150° (Baeyer, *A.* 202, 136). Slender yellow needles; its alcoholic solution shows reddish fluorescence. Its solution in alkalis is reddish-brown. NaOH at 200° gives alizarin.

Acetyl derivative $C_{14}H_5AcBr_2O_3$. [190°].

Di-bromo-di-oxy-anthraquinone $C_{14}H_4O_2(OH)_2Br_2$. *Di-bromo-alizarin.* [170°]. Prepared by the action of Br in presence of I on alizarin. Small brownish-red needles. Combines with mordants (Diehl, *B.* 11, 190).

Di-bromo-di-oxy-anthraquinone $C_{14}H_4O_2(OH)_2Br_2$. *Di-bromo-purpuroxanthin.* [227°-230°] (P.); [231°] (S. a. R.). From purpuroxanthin and Br (Plath, *B.* 9, 1205). From munjistin and Br (Schunck a. Roemer, *C. J.* 33, 424). Orange needles (from HOAc). Warm conc. H_2SO_4 forms bromo-purpurin.

Salt.—$(NH_4)_2A''$.

Tri-bromo-tri-oxy-anthraquinone $C_{14}H_2O_2(OH)_3Br_3$. *Tri-bromo-flavopurpurin.* [284°]. From flavopurpurin in HOAc and Br. Orange needles. Its alkaline solutions are orange (Schunck a. Roemer, *B.* 10, 1225).

Tetra-bromo-di-oxy-anthraquinone $C_{14}H_2O_2(OH)_2Br_4$. *Tetra-bromo-alizarin.* From alizarin and excess of iodine bromide at 180°. Does not combine with mordants (Diehl, *B.* 11, 191).

BROMO-o-OXY-BENZOIC ACID $C_7H_5BrO_3$ *i.e.* $C_6H_3Br(OH)CO_2H$ [3:2:1]. *Bromo-salicylic acid.* [184°] (L. a. G.); [220°] (H. a. E.). From the corresponding bromo-amido-benzoic acid by exchange of NH_2 for OH (Hübner a. Emmerling, *Z.* 1871, 709) or from (3, 5, 2, 1)-bromo-amido-oxy-benzoic acid by eliminating NH_2 (Lellmann a. Grothmann, *B.* 17, 2725). Needles, v. sl. sol. cold water, v. e. sol. alcohol. Fe_2Cl_6 gives a violet colouration.—CaA'_2 12aq: v. sol. water. BaA'_2 3½aq: prisms.—PbA'_2 (H.).—$PbC_7H_3BrO_3$.

Bromo-o-oxy-benzoic acid $C_6H_3Br(OH)(CO_2H)$ [5:2:1]. [165°]. From salicylic acid and Br or PBr_5 (Gerhardt, *A. Ch.* [3] 7, 217; Cahours, *A. Ch.* [3] 10, 341; 13, 99; Henry, *B.* 2, 275; H. a. E.). Also from the corresponding amido-*m*-bromo-benzoic acid (H. a. E.). Needles (from water). Fe_2Cl_6 gives a violet colouration. BaA'_2 3aq.—PbA'_2. $PbC_7H_3BrO_3$.—CuA'_2.—AgA'.

Methyl ether MeA'. [38°] (Henry); [61°] (Peratoner, *G.* 16, 405). (265°). From methyl salicylate and Br or PBr_5. Trimetric prisms or needles. Coloured violet by Fe_2Cl_6.

Methyl derivative $C_6H_3Br(OMe)CO_2H$. [119°]. — BaA'_2 3aq. — CaA'_2 4aq. AgA'aq. Methyl ether $C_6H_3Br(OMe)CO_2Me$. [40°]. (295°) (P.).

Ethyl derivative $C_6H_3Br(OEt)CO_2H$. [130°]. BaA'_2 4aq.—CaA'_2 2aq. Methyl ether $C_6H_3Br(OEt)CO_2Me$. [49°]. (301°).

Propyl derivative $C_6H_3Br(OPr)CO_2H$. [62°]. Methyl ether $C_6H_3Br(OPr)CO_2Me$. (323°).

Isopropyl derivative $C_6H_3Br(OPr)CO_2H$. [101°]. Methyl ether (301°).

Bromo-*p*-oxy-benzoic acid. *Methyl derivative* $C_6H_3Br(OMe)CO_2H$ [3:4:1]. *Bromo-anisic acid.* [214°]. [218° cor.].

Formation.—1. From anisic acid and Br (Laurent; Cahours, *A.* 56, 311; Salkowski, *B.* 7, 1013).—2. By oxidising the methyl ether of bromo-*p*-cresol (Schall a. Dralle, *B.* 17, 2531).

Properties.—Needles; may be distilled or sublimed. Insol. water.

Salts.—AgA'.—BaA'_2 3½aq.—BaA'_2 4aq.—CaA'_2 6aq.—CuA'_2 2½aq.—MgA'_2 5aq.—NaA'_2 2aq.—PbA'_2 3aq.—ZnA'_2 3aq.

Ethyl ether $C_6H_3Br(OMe)(CO_2Et)$. [74°] (Crespi, *G.* 11, 419).

Amide $C_6H_3Br(OMe)(CO_2NH_2)$. [186°]; insol. water.

Bromo-*p*-oxy-benzoic acid. *Methyl derivative* $C_6H_3Br(OMe)CO_2H$. [212°]. Ethyl bromo-anisate [74°] is converted into an isomeride [60°] by heating with NaOEt at 180° for 20 hours; on saponification it yields the acid which crystallises in needles, sl. sol. water. Potash fusion forms protocatechuic acid. HNO_3 gives the methyl ether of (2,4,6,1)-bromo-di-nitro-phenol.

Salt.—ZnA'_2 4aq (Balbiano, *G.* 11, 409).

Ethyl ether EtA'. [60°] (*v. supra*). This acid is possibly identical with the preceding.

Bromo-di-oxy-benzoic acid. *Methyl derivative* $C_6H_2Br(OH)(OMe)CO_2H$ [x:4:3:1]. *Bromo-vanillic acid.* [193°]. From its acetyl derivative. Needles (containing aq). Acetyl derivative $C_6H_2Br(OAc)(OMe)CO_2H$. [167°]. From acetyl-vanillic acid and Br (Matsmoto, *B.* 11, 138).

Di-methyl derivative $C_6H_2Br(OMe)_2CO_2H$ [x:4:3:1]. *Bromo-veratric acid.* [184°]. From veratric acid and Br (M.).

Methylene derivative $C_6H_2Br(O_2CH_2)CO_2H$ or $C_6H_3(O_2CHBr)CO_2H$. *Bromo-piperonylic acid,* [205°]. From bromo-piperonal and $KMnO_4$ (Fittig a. Mielck, *A.* 172, 158).

Bromo-di-oxy-benzoic acid $C_6H_2Br(OH)_2CO_2H$ [x:1:3:5]. [253°]. From s-di-oxy-benzoic acid and bromine water (Barth a. Senhofer, *A.* 164, 115). Needles (containing aq). Potash-fusion forms gallic acid. Fe_2Cl_6 gives a yellowish-brown colour.—CaA'_2 8aq.—Ag_2A''.

Bromo-di-oxy-benzoic acid $C_6H_2Br(OH)_2CO_2H$ [x:2:6:1]. [184°, anhydrous]. From c-di-oxy-benzoic acid in ether and Br (Zehenter, *M.* 2, 480). Prisms (containing aq). Fe_2Cl_6 gives a violet colour to its aqueous solution.—AgA'aq. BaA'_2 7½aq.—CuA'_2 4½aq.—PbA'_2 3aq.—KA' 1½aq.

Bromo-tri-oxy-benzoic acid $C_6HBr(OH)_3CO_2H$. *Bromo-gallic acid.* [above 200°]. From gallic acid and Br (Hlasiwetz, *A.* 142, 250; Grimaux, *Z.* 1867, 431). Monoclinic; sl. sol. water.

Di-bromo-o-oxy-benzoic acid $C_6H_2Br_2(OH)CO_2H$ [5:3:2:1]. *Di-bromo-salicylic acid.* [219°] (R.); [223°] (L. a. G.). From salicylic acid and Br or from (3,5,2,1)-bromo-amido-salicylic acid by the diazo- reaction (Cahours, *A. Ch.* [3] 10, 339; 13, 102; Rollwage, *B.* 10, 1707; Lellmann a. Grothmann, *B.* 17, 2727). Gives a violet colour with Fe_2Cl_6. Heated with dilute H_2SO_4 it gives (3,5,2)-di-bromo-phenol [36°].—BaA'_2 4aq.

Methyl ether $C_6H_2Br_2(OH)CO_2Me$: [149°]; from methyl salicylate and Br (Peratoner, *G.* 16, 405). Long needles, sl. sol. alcohol.

Methyl derivative $C_6H_2Br_2(OMe)CO_2H$: [194°].—Salt BaA'_2 2½aq. Methyl ether $C_6H_2Br_2(OMe)CO_2Me$: [53°]; needles.

Ethyl derivative $C_6H_2Br_2(OEt).CO_2H$: [156°]; white needles. Methyl ether $C_6H_2Br_2(OEt).CO_2Me$: [43°]; needles.

Di-bromo-o-oxy-benzoic acid $C_6H_2Br_2(OH)CO_2H$ [4:3:2 or 6:1]. [218°]. From (4,3,1)-di-bromo-benzoic acid [229°] by nitration, reduction, and diazotisation (Smith, *B.* 10, 1706). Gives a violet colour with Fe_2Cl_6.

Di-bromo-o-oxy-benzoic acid $C_6H_2Br_2(OH)CO_2H$. [221°]. Formed as a by-product in converting (5,2,1)-bromo-nitro-benzoic acid [250°] into di-bromo-benzoic acid by the diazo- reaction (Hübner a. Lawrie, *B.* 10, 1706). Fe_2Cl_6 gives a violet colour.

Di-bromo-p-oxy-benzoic acid $C_6H_2Br_2(OH)CO_2H$. [268°]. From di-bromo-anisic acid and conc. HI (Alecci, *G.* 15, 242). One of the products of the dry distillation of sodium di-bromo-anisate (Balbiano, *G.* 13, 69). Long needles, insol. water, sol. alcohol and ether. Fe_2Cl_6 turns its solutions yellowish-red. Sodium-amalgam forms p-oxy-benzoic acid.—CaA'_2 3aq.

Methyl derivative $C_6H_2Br_2(OMe)CO_2H$ [3:5:4:1]. *Di-bromo-anisic acid* [207°] (R.); [214°] (C.). From anisic acid, Br, and water at 120° (Reinecke, *Z.* 1866, 366; Crespi, *G.* 11, 425). Converted by prolonged action of Br and water into tri-bromo-anisol [87°].—NaA' 3aq.—AgA'.—BaA'_2 4½aq. Ethyl ether $C_6H_2Br_2(OMe)(CO_2Et)$: [88°]; plates.

Di bromo-di-oxy-benzoic acid $C_6HBr_2(OH)_2CO_2H$. [214°]. From (3, 2, 1)-di-oxy-benzoic acid and Br (Zehenter, *M.* 2, 475). Needles (containing aq); m. sol. hot water. Fe_2Cl_6 turns its solution violet; conc. H_2SO_4 gives a green colour. Heating with water forms di-bromo-resorcin.—KA' 3½aq.—CaA'_2 8½aq.—$PbC_7H_2Br_2O_4$.—CuA'_2 aq.—AgA'.

Di-bromo-tri-oxy-benzoic acid $C_6Br_2(OH)_3CO_2H$. *Di-bromo-galli acid.* [140°] (G.); [150°] (E.). From gallic acid and Br (Grimaux, *Z.* 1867, 431; Etti, *B.* 11, 1882). Fe_2Cl_6 gives a blue-black colour in its aqueous solution.

Tri-bromo-o-oxy-benzoic acid $C_6HBr_3(OH)CO_2H$. *Tri-bromo-salicylic acid.* From Br and salicylic acid. Small prisms, insol. water (Cahours, *A. Ch.* [3] 13, 104).

Tri-bromo-m-oxy-benzoic acid $C_6HBr_3(OH)CO_2H$. [147°]. From m-oxy-benzoic acid (1 mol.) and Br (3 mols.) (Werner, *Bl.* [2] 46, 276).

Tri-bromo-di-oxy-benzoic acid $C_6Br_3(OH)_2CO_2H$. [183°]. From (5, 3, 1)-di-oxy-benzoic acid and Br (Barth a. Senhofer, *A.* 159, 225). Tables (from water). Potash-fusion reproduces s-di-oxy-benzoic acid.

BROMO-o-OXY-BENZOIC ALDEHYDE $C_7H_5BrO_2$ *i.e.* $C_6H_3Br(OH)CHO$. *Bromo-salicylic aldehyde.* [99°]. From salicylic aldehyde and Br or PBr_5 (Löwig, *P.* 46, 57, 383; Piria, *A. Ch.* [2] 69, 281; Henry, *B.* 2, 275). Laminæ; insol. water, sol. alcohol and ether. Combines with $KHSO_3$.

Methyl derivative $C_6H_3Br(OMe)CHO$. [114°]. From methyl-salicylic aldehyde and Br (Perkin, *A.* 145, 304). Flat prisms (from alcohol).

Ethyl derivative $C_6H_3Br(OEt)CHO$: [68°]; prisms.

Bromo-p-oxy-benzoic aldehyde $C_6H_3Br(OH)CHO$. [180°]. From p-oxy-benzoic aldehyde and Br. V. sol. alcohol and ether, v. sl. sol. water: Combines with $KHSO_3$ (Herzfeld, *B.* 10, 2198).

Di-bromo-o-oxy-benzoic aldehyde $C_6H_2Br_2(OH)CHO$. *Di-bromo-salicylic-aldehyde.* Prisms. From salicylic aldehyde and Br (Heerlein, *J. pr.* 32, 65).

Phenyl-hydrazide $C_6H_2Br_2(OH)CH:N_2HPh$: [148°]; v. sol. alcohol, benzene, ether, and $CHCl_3$, insol. water. The mono-acetyl-derivative $C_6H_2Br_2(OAc)CH:N_2HPh$ forms fine needles [188°], nearly insoluble in ether. The di-acetyl derivative $C_6H_2Br_2(OAc)CH:N_2AcPh$ crystallises in white needles, [158°], easily soluble in ether; it is formed by brominating the di acetyl derivative of the phenyl-hydrazide of salicylic aldehyde (Rossing, *B.* 17, 3008).

Di-bromo-p-oxy-benzoic aldehyde $C_6H_2Br_2(OH)CHO$. [181°]. From p-oxy-benzoic

aldehyde (1 mol.) and Br (2 mols.) (Werner, *Bl.* [2] 46, 277).

BROMO-OXY-BUTYRIC ACID $C_4H_7BrO_3$. [102°]. From di-bromo-butyric acid and baryta. Laminæ (Petrieff a. Eghis, *J. R.* 7, 179).—BaA'_2.—AgA'.

Bromo-oxy-butyric acid $CH_3.CHBr.CH(OH)CO_2H$ or $CH_3.CH(OH).CHBr.CO_2H$. An uncrystallisable syrup obtained as a residue when $\alpha\beta$-di-bromo-butyric acid is distilled with water (C. Kolbe, *J. pr.* 133, 389; *cf.* Erlenmeyer a. Müller, *B.* 15, 49).

Bromo-oxy-butyric acid $CH_3.CHBr.CH(OH).CO_2H$ or $CH_3.CH(OH).CHBr.CO_2H$. [90°]. From β-methyl-glycidic acid $O<\begin{matrix}CH.CH_3\\CH.CO_2H\end{matrix}$ and HBr (Melikoff, *Bl.* [2] 43, 116). Prisms. Probably identical with the preceding.

Bromo-oxy-iso-butyric acid $CH_2Br.C(OH)Me.CO_2H$. [101°]. Formed by boiling di-bromo-iso-butyric acid with water, and extracting with ether (K.). Also from HBr and α-methyl-glycidic acid $O<\begin{matrix}CH_2\\CMe.CO_2H\end{matrix}$. Needles; sol. hot benzene, insol. $CHCl_3$ and CS_2. Not affected by boiling water. Reduced by the action of sodium amalgam on its aqueous solution, kept neutral by H_2SO_4, to oxy-iso-butyric acid, [79°].

BROMO-OXY-CINNAMIC ACID *v.* BROMO-COUMARIC ACID.

BROMO-(*B.* 4)-OXY-(*Py.* 4)-ETHYL-QUINOLINE TETRA-HYDRIDE $C_9H_8Br(OH)EtN$.

Ethyl ether [35°]; long monoclinic prisms, $a:b:c = 0.7902:1:0.5828$. Formed by bromination of ethyl-kairine (ethyl ether of oxy-ethyl-quinoline-tetra-hydride), or by ethylation of the ethyl-ether of bromo-oxy-quinoline-tetra-hydride. The picrate forms yellow needles [174°] (Fischer a. Renouf, *B.* 17, 762).

DI-BROMO-OXY-INDONAPHTHENE $C_9H_4Br_2O$ *i.e.* $C_6H_4<\begin{matrix}CO\\CBr\end{matrix}>CBr$. *Phenylene-di-bromo-acetylene ketone.* [123°]. Obtained by heating di-bromo-cinnamic acid $C_6H_5.CBr:CBr.CO_2H$ with conc. H_2SO_4. Yellow needles.

Oxim $C_9H_4Br_2(NOH)$: [195°]; yellow needles.

Anilide: [170°]; red needles.

Di-bromide $C_9H_4OBr_4$: [124°]; prisms (Roser, *B.* 20, 1273).

BROMO-OXY-MALEÏC ACID *Phenyl derivative* $CO_2H.CBr:C(OPh).CO_2H$. [104°]. From the phenyl derivative of oxy-mucobromic acid and Ag_2O (Hill a. Stevens, *Am.* 6, 187). Needles. —Ag_2A''.

***p*-BROMO-ω-OXY-MESITYLENE** $C_9H_{11}BrO$ *i.e.* $C_6H_2(CH_3)_2Br(CH_2.OH)$ [5:3:4:1]. *p-Bromo-mesityl alcohol.* [66°]. Obtained from p-ω-di-bromo-mesitylene (p-mesityl bromide) by treatment with KOAc and saponification of the acetate. Pointed needles. V. e. sol. alcohol, ether, and benzene, sl. sol. cold petroleum-ether, insol. cold water. Decomposes on distillation with separation of H_2O and formation, amongst other products, of p-bromo-mesitylenic aldehyde $C_6H_2(CH_3)_2Br(CHO)$. By oxidising agents it is readily converted into p-bromo-mesitylenic acid [214°] (Schramm, *B.* 19, 213).

***eso*-Bromo-$\omega_1\omega_2$-di-oxy-mesitylene** $C_6H_2Br(CH_3)(CH_2OH)_2$. [121°]. S. 3½ at 100°. From the corresponding tri-bromo-mesitylene (200°–215°) by boiling with water and $PbCO_3$ (Colson, *A. Ch.* [6] 6, 98; *C. R.* 97, 177). Pearly scales; v. sl. sol. cold water, m. sol. alcohol. Boiling HClAq forms $C_6H_2Br(CH_3)(CH_2Cl)_2$ [75°].

BROMO-OXY-β-METHYL-CUMARILIC ACID
$C_6H_2Br(OH)\overset{(4)}{}<\begin{matrix}\overset{(1)}{C}Me\\ \scriptstyle(2)\\O\end{matrix}>C.CO_2H$. [221°]. Formed by boiling bromo-β-methyl-umbelliferon-di-bromide $C_6H_2Br(OH)<\begin{matrix}CMeBr.CHBr\\ |\\O\text{———}CO\end{matrix}$ with alcoholic KOH. Colourless needles. V. sol. alcohol and ether, sl. sol. benzene, insol. water. Cold H_2SO_4 gives a colourless solution which becomes violet on heating. Fe_2Cl_6 gives a yellow colouration with the alcoholic solution (Pechmann a. Cohen, *B.* 17, 2134).

BROMO-OXY-METHYL-ETHYL-PYRIMIDINE $C_2H_5.C<\begin{matrix}N.C(OH)\\N:C(CH_3)\end{matrix}>CBr$. [195°]. Formed by bromination of oxy-methyl-ethyl-pyrimidine. Long colourless glistening needles. Sl. sol. water. $C_7H_9N_2Br(OH)aq$: very soluble long white needles (Pinner, *B.* 20, 2362).

BROMO-OXY-DI-METHYL-PYRIMIDINE $CH_3.C<\begin{matrix}N.C(OH)\\N:C(CH_3)\end{matrix}>CBr$. Formed by bromination of oxy-di-methyl-pyrimidine. The hydrobromide (B'HBr) forms colourless needles, m. sol. water, v. sol. alcohol (Pinner, *B.* 20, 2361).

(*Py.* 2,3,1)-BROMO-OXY-METHYL-QUINOLINE
$C_{10}H_8NOBr$ *i.e.* $C_6H_4<\begin{matrix}CMe:CBr\\ \quad |\\N\ :\ C.OH\end{matrix}$? *Bromo-oxyquinaldine, or bromo-quinoxyl.* [c. 258°]. Formed by the action of cold conc. H_2SO_4 upon the anilide of bromo-aceto-acetic acid $CH_3.C(OH):CBr.CONHPh$. Also from (*Py.* 3,1)-oxy-methyl-quinoline and bromine-water (Knorr, *B.* 17, 2875; *A.* 236, 91). Fine silky needles. Sl. sol. alcohol, ether, and chloroform. Dissolves in aqueous acids and alkalis.

Tri-bromo-(*Py.*1)-oxy-(*Py.*3)-methyl-quinoline $C_9H_2MeBr_3(OH)N$. [275°]. Formed by bromination of (Py. 1, 3)-oxy-methyl-quinoline. Insol. alcohol (Conrad a. Limpach, *B.* 20, 949).

Bromo-(*Py.*3)-oxy-(*Py.*1,4)-di-methyl-quinoline $C_{11}H_{10}BrNO$. *Bromo-methyl-lepidone.* [172°]. From the corresponding oxy-dimethyl-quinoline and bromine-water (Knorr, *A.* 236, 110). Spherical aggregates of needles (from alcohol). Insol. water and NaOHAq, v. sol. dilute acids.

BROMO-OXY-(α)-NAPHTHOIC ANHYDRIDE
$C_{11}H_5BrO_2$ *i.e.* $C_{10}H_5Br<\begin{matrix}CO\\ |\\O\end{matrix}$ [192°]. Formed by bromination of oxy-naphthoic anhydride $C_{10}H_6<\begin{matrix}CO\\ |\\O\end{matrix}$ dissolved in CS_2. Small white needles (Ekstrand, *B.* 19, 1139).

Bromo-oxy-(α)-naphthoquinone
$C_6H_4<\begin{matrix}CO.C(OH)\\ \|\\CO.CBr\end{matrix}$. [197°].

Formation.—1. From di-bromo-(α)-naphthoquinone [151°] by boiling with aqueous NaOH

or Na_2CO_3; the yield being 60 p.c. of the theoretical (Diehl a. Merz, *B.* 11, 1064).—2. From oxy-(a)-naphthoquinone and Br.—3. Prepared by the action of alcoholic H_2SO_4 on di-bromo-(a)-naphthoquinone-anilide, *p*-bromo-aniline being simultaneously produced (Baltzer, *B.* 14, 1901). 4. By the action of alkali upon bromo-β-naphthoquinone (Zincke a. Gerland, *B.* 20, 1515).—5. By boiling bromo-amido-(a)-naphthoquinone $C_6H_4<\substack{CO.C(NH_2)\\ CO.CBr}$ with dilute alkalis (Z.).—6. From bromo-oxy-(a)-naphthoquinone-imide $C_6H_4<\substack{CO - C(OH)\\ C(NH).CBr}$ by boiling with conc. HCl or by treatment with alcoholic NaOH (Z.).

Properties.—Yellow needles; v. sl. sol. water, sl. sol. ether, v. sol. alcohol. Oxidation gives phthalic acid.

Salts.—KA'aq: red needles.—BA'_2. S. ·07 at 13°.—AgA'.

Bromo-oxy-(a)-naphthoquinone. [202°]. From the anilide [197°] of di-bromo-naphthoquinone [218°] by boiling with aqueous Na_2CO_3 (Miller, *Bl.* [2] 43, 125). Oxidises to phthalic acid; it should therefore be identical with the preceding.

BROMO - OXY - (a) - NAPHTHOQUINONE - IMIDE $C_6H_4<\substack{CO - C(OH)\\ | \\ C(NH).CBr}$. [c. 265°]. Formed by boiling bromo-amido-(a)-naphthoquinone-imide $C_6H_4<\substack{CO - C(NH_2)\\ C(NH).CBr}$ with dilute NaOH. Formed also by the action of NH_3 upon bromo-(β)-naphthoquinone. Brownish-red glistening needles. By boiling with conc. HCl or by treatment with alcoholic NaOH it is converted into bromo-oxy-(a)-naphthoquinone. The sodium-salt forms red needles; the salts of the heavy metals are sparingly soluble pps.

Acetyl derivative: [270°]; red hair-like needles (Zincke a. Gerland, *B.* 20, 1514).

BROMO-OXY-NAPHTHOQUINONE SULPHONIC ACID $C_{10}H_5BrSO_6$ *i.e.* $C_{10}H_3O_2Br(OH)(SO_3H)$. From (β)-naphthol sulphonic acid and Br, di-bromo oxy-naphthoquinone being also formed in small quantity (Armstrong a. Graham, *C. J.* 39, 138; Armstrong a. Streatfeild, *C. J. Proc.* 1, 232).—$BaC_{10}H_3BrSO_6$.

BROMO-OXY-NICOTINIC ACID *v.* BROMO-OXY-PYRIDINE CARBOXYLIC ACID.

BROMO-OXY-OCTOIC ACID $C_8H_{15}BrO_3$ *i.e.* $CH_3.CHBr.CH_2.CH(CO_2H).CH_2.CH(OH).CH_3$. *Bromo-oxy-di-propyl-acetic acid.*

Lactone $CH_3.CHBr.CH_2.CH<\substack{CH_2.CH.CH_3\\ | \\ CO.O}$. S.G. $\frac{15}{}$ 1·394. From di-allyl-acetic acid and HBr, the compound $(CH_3.CHBr.CH_2)_2CH.CO_2H$ being probably first formed (Hjelt, *A.* 216, 73). Oil. Insol. cold water, v. sl. sol. warm water. Insol. cold NaOH. Boiled for a long time with water or aqueous Na_2CO_3 it appears to form the lactone $CH_2:CH.CH_2.CH<\substack{CH_2.CHMe\\ | \\ CO.O}$ *v.* OXY-OCTENOIC ACID.

Tri-bromo-oxy-octoic acid. *Lactone* $CH_2Br.CHBr.CH_2.CH<\substack{CH_2.CH.CH_2Br\\ | \\ CO.O}$ From di-allyl-acetic acid and bromine in chloroform (Hjelt, *A.* 216, 76). Oil. V. sol. ether. Insol. cold NaOHAq. Boiled with aqueous Na_2CO_3 it forms $(CH_2(OH).CH(OH).CH_2)_2CH.CO_2Na$.

Tri-bromo-di-oxy-octoic acid. *Lactone* $C_8H_{11}Br_3O_3$ *i.e.* $CH_2Br.CHBr.CH_2.C(OH).CH_2.CH(CH_2Br).O.CO$. From so-called 'di-allyl-oxalic acid' and bromine (*v.* OXY-OCTINOIC ACID) (Schatzky, *J. pr.* [2] 34, 485).

Tetra-bromo-oxy-octoic acid $C_8H_{12}Br_4O_3$ *i.e.* $(CH_2Br.CHBr.CH_2)_2C(OH).CO_2H$. From so-called 'di-allyl-oxalic acid' and Br (Saytzeff, *A.* 185, 189). Oil: readily splits up into HBr and the preceding lactone.

Ethyl ether EtA'. Oil (Schatzky, *J. R.* 17, 73).

DI - BROMO - HEXA - OXY - DIPHENYL. *Methyl ether* $C_{12}H_2Br_2(OMe)_6$. [140°]. From the methyl ether of hexa-oxy-diphenyl and Br (Ewald, *B.* 11, 1623). Needles (from alcohol or HOAc); conc. H_2SO_4 forms a blue solution.

Tetra-bromo-di-oxy-diphenyl $C_{12}H_6Br_4O_2$ *i.e.* $C_6H_2Br_2(OH).C_6H_2Br_2(OH)$. [264°]. From di-oxy-diphenyl and Br (Magatti, *B.* 11, 2267; 13, 225). Also by reduction of bromo-rosoquinone (Baeyer, *B.* 11, 1301). Fuming HNO_3 forms brownish-red scales of $(C_6H_2Br_2O)_2$. '*Tetra-bromo-diphenyl-quinone.*'

Acetyl derivative $C_{12}H_4Ac_2Br_4O_2$. [245°]; needles.

Tetra-bromo-tetra-oxy-diphenyl $C_{12}H_2Br_4(OH)_4$. *Tetra-bromo-diresorcin.* From tri-bromo-resoquinone $C_6HBr_3O_2$(?) and H_2S or Sn and HCl. Needles (from HOAc). Turns brown at 230° and decomposes at 280°. Insol. water, v. sol. alcohol and ether. Sodium-amalgam gives diresorcin. Red-hot zinc-dust gives diphenyl.

Acetyl derivative $C_{12}H_2Br_4(OAc)_4$. [195°]; needles (from alcohol) (Benedikt, *M.* 1, 352; *B.* 11, 2170).

Deca-bromo-tetra-oxy-diphenyl $C_{12}Br_6(OBr)_4$. Formed by adding Br and HCl to a solution of diresorcin in aqueous potash (Benedikt a. Julius, *M.* 5, 179). Unstable crystals, gives off Br (2 mols.) at 185°. SO_2 reduces it to $C_{12}Br_6(OH)_4$.

BROMO-*p*-OXY-PHENYL-ACETYLENE. *Methyl derivative* $C_6H_3Br(OMe).C{:}CH$. [75°]. Formed by heating the methyl derivative of tri-bromo-*p*-oxy-phenyl-propionic acid $C_6H_3Br(OMe).CHBr.CHBr.CO_2H$ with aqueous KOH (30 p.c.). Plates. Gives an unstable greenish-yellow compound with ammoniacal $CuCl_2$ (Eigel, *B.* 20, 2538).

DI-BROMO-DI-OXY-DI-PHENYL-AMINE $C_6H_4(OH).NH.C_6H_2Br_2.OH$ [4:6:2:1]. *Leuco-di-bromo-quinone-phenol-imide.* [170°]. Colourless prisms. V. sol. all ordinary solvents, except water. Formed by reduction of di-bromo-quinone phenol-imide (Möhlau, *B.* 16, 2848).

a - β - eso - eso - **TETRA - BROMO - *o* - OXY - β - PHENYL-BUTYRIC ACID.** *Methyl derivative* $C_6H_2Br_2(OMe).CHBr.CMeBr.CO_2H$. [c. 200°]. From (a) or (β) methoxy-phenyl-crotonic acid and bromine vapour (Perkin, *C. J.* 39, 434). Crystalline powder (from chloroform).

Tetra-bromo-di-oxy-di-phenyl-methane $C_{13}H_8Br_4O_2$ *i.e.* $CH_2(C_6H_2Br_2.OH)_2$. [225°]. From di-oxy-di-phenyl-methane and bromine-water

In ethereal solution it forms an unstable crystalline compound with hydric bromide $C_{13}H_9Br_5O_2$ (Beck, *B.* 10, 1837).

BROMO-OXY-PHENYL-METHYL-PYRAZOLE $C_6H_5.N\langle{}^{CO-CHBr}_{N=CMe}\rangle$. *Bromo-phenyl-methyl-pyrazolone.* [c. 130°]. From oxy-phenyl-methyl-pyrazole and Br in glacial acetic acid (Knorr, *A.* 238, 176). Sol. alkalis, and dilute acids; insol. water. Sl. sol. ether, v. sol. glacial HOAc and chloroform. In alcoholic solution it slowly forms pyrazole-blue. Fe_2Cl_6 forms pyrazole-blue.

Di-bromo-oxy-phenyl-methyl-pyrazole $C_{10}H_8N_2OBr_2$ *i.e.* $PhN\langle{}^{CO-CBr_2}_{N=CMe}\rangle$. *Di-bromo-phenyl-methyl-pyrazolone.* [80°]. From oxy-phenyl-methyl-pyrazole (1 pt.) and Br (2 pts.) in acetic acid solution (Knorr, *A.* 238, 177). Sol. alcohol, HOAc, ether, and $CHCl_3$; insol. water, alkalis, and acids. Not attacked by Fe_2Cl_6. Reduced by Sn and HCl or fuming HI to oxy-phenyl-methyl-pyrazole.

BROMO-OXY-PHENYL-METHYL-PYRIMIDINE $C_{11}H_9N_2BrO$ *i.e.* $C_6H_5.C\langle{}^{N.C(OH)}_{N:C(CH_3)}\rangle CBr$. [260°]. Formed by bromination of oxy-phenyl-methyl-pyrimidine. Glistening needles (Pinner, *B.* 20, 2361).

BROMO-o-OXY-PHENYL-PROPIOLIC ACID.
Methyl derivative
$C_6H_3(OMe)Br.C:C.CO_2H$. [168°] (with decomposition). From the methyl derivative of tri-bromo-oxy-phenyl-propionic acid (*q.v.*). Short white needles (from benzene).

BROMO-o-OXY-β-PHENYL-PROPIONIC ACID $C_9H_9BrO_3$ *i.e.* $C_6H_3Br(OH).CH_2.CH_2.CO_2H$. *Bromo-melilotic acid.* [142°]. From its anhydride by boiling with water. Rectangular tables (from chloroform). Sol. alcohol, sl. sol. water. Changes on melting into its anhydride.

Anhydride $C_6H_3Br\langle{}^{O}_{CH_2.CH_2}\rangle CO$. [106°]. From melilotic anhydride and Br in CS_2 in the cold (Fittig a. Hochstetter, *A.* 226, 361). Thick prisms (from chloroform). Bromine is not taken out by boiling alkalis. Sol. alcohol and chloroform, sl. sol. CS_2. Slowly converted by boiling water into bromo-melilotic acid.

α-Bromo-β-oxy-β-phenyl-propionic acid $C_6H_5.CH(OH).CHBr.CO_2H$. [122°]; [125°, anhydrous]. From αβ-di-bromo-β-phenyl-propionic acid by boiling with water (Glaser, *A.* 147, 81). Thin laminæ (containing aq). Boiled with very dilute Na_2CO_3 it gives phenyl-acetic aldehyde:

$$Ph.CH(OH).CHBr.CO_2H = Ph.CH\,.\,CH.CO_2H + HBr = $$
$$\quad\setminus O /$$
$$Ph.CH.CH(OH) + HBr =$$
$$\;O\,.\,CO$$
$$Ph.CH:CH.OH + CO_2 + HBr = Ph.CH_2.CHO + CO_2 + HBr.$$

The yield is 75 p.c. of the theoretical, but some phenyl-glyceric acid is also formed:

$$Ph.CH\,.\,CH.CO_2H + H_2O =$$
$$\quad\setminus O /$$
$$Ph.CH(OH).CH(OH).CO_2H$$

(Erlenmeyer, *B.* 13, 308). Salt.—AgA'.

ββ-Bromo-α-oxy-α-phenyl-propionic acid $CHBr_2.CPh(OH).CO_2H$. *Di-bromo-atrolactic acid.* [167°]. Prepared by dissolving di-bromo-pyruvic acid and benzene in cold H_2SO_4. Long needles or four-sided tables. Sol. benzene and CS_2, sl. sol. cold water. By boiling with water it decomposes into CO_2, HBr, and ω-brom-acetophenone ($C_6H_5.CO.CH_2Br$). On reduction it gives atrolactic acid (Böttinger, *B.* 14, 1235).

Bromo-di-oxy-phenyl-propionic acid
Methylene ether $C_{10}H_9BrO_4$ or $CH_2\langle{}^{O}_{O}\rangle C_6H_2Br.CH_2.CH_2.CO_2H$. *Bromo-pipero-propionic acid.* [140°]. From sodium bromo-(β)-hydro-piperate and $KMnO_4$ (Weinstein, *A.* 227, 44). Monoclinic crystals (from ether) sol. alcohol, sl. sol. water.—CaA'_2.

Di-bromo-o-oxy-phenyl-propionic acid $C_9H_8Br_2O_3$. *Di-bromo-melilotic acid.* [115°]. From melilotic acid and Br (Zwenger, *A. Suppl.* 5, 116). Needles; may be distilled.—BaA'_2 5aq

α-β-Di-bromo-o-oxy-phenyl-propionic acid. *Di-bromide of coumaric acid.*
Methyl derivative
$C_6H_4(OMe).CHBr.CHBr.CO_2H$. [162°]. S. ($CHCl_3$) 2·7 at 17°. From the methyl derivative of coumaric acid $C_6H_4(OMe)CH:CH.CO_2H$ and Br. V. sol. ether. Decomposed by aqueous alkalis. With bromine vapour it gives rise to $C_6H_2Br_2(OMe)CHBr.CHBr.CO_2H$ [c. 202°]. Crystals (from benzene) (Perkin, *C. J.* 39, 420; Fittig a. Ebert, *A.* 216, 157). Strong potash (1:1) forms $C_6H_4(OMe)C_2HBr.CO_2H$ [171°].
Di-methyl ether
$C_6H_4(OMe)CHBr.CHBr.CO_2Me$.
(α)-compound [125°]. S. (CS_2) 3·4.
(β)-compound [68°]. S. (CS_2) ·4.
These two compounds are formed together by acting on the isomeric methoxy-phenyl-acrylates of methyl with bromine in CS_2. But the (α)-isomeride gives chiefly that melting at 125° while the (β)-isomeride forms chiefly the other (Perkin *C. J.* 39, 424). Alcoholic potash converts both into methoxy-phenyl-bromo-acrylic acid.
Ethyl derivative
$C_6H_4(OEt).CHBr.CHBr.CO_2H$. [155°]. S. ($CS_2$) 1·03 at 18°. From the ethyl derivatives of coumaric and of coumarinic acids by Br (F. a. E.). Small crystals (from CS_2).
Di-ethyl ether
$C_6H_4(OEt)CHBr.CHBr.CO_2Et$. [78°]. From $C_6H_4(OEt)CH:CH.CO_2Et$ and Br in CS_2 (P.).

eso-Di-bromo-p-oxy-β-phenyl-propionic acid $HO.C_6H_2Br_2.CH_2.CH_2.CO_2H$. *Di-bromo-hydro-p-coumaric acid.* [108°]. From aqueous hydro-p-coumaric acid and cold bromine-water (Stöhr, *A.* 225, 64). Needles (from acetic acid).
Salts.—$(NH_4)_2C_9H_6Br_2O_3$.—$Ag_2C_9H_6Br_2O_3$.

αβ-Di-bromo-p-oxy-phenyl-propionic acid $C_6H_4(OH).CHBr.CHBr.CO_2H$. *p-Coumaric-acid-di-bromide.*
Methyl derivative
$C_6H_4(OMe).CHBr.CHBr.CO_2H$: [149°]; colourless crystals. Formed by combination of the methyl derivative of p-coumaric acid with Br.
Di-methyl ether
$C_6H_4(OMe).CHBr.CHBr.CO_2Me$: [118°]; m. sol. ether and chloroform. Formed by combination of the di-methyl ether of p-coumaric acid with bromine. When boiled with aqueous

potash solution (30 p.c.) it is converted into the methyl derivative of ω-bromo-*p*-vinyl-pheno $C_6H_4(OMe).CH:CHBr$ (Valentini, *G.* 16, 424 Eigel, *B.* 20, 2536).

Di-bromo-di-*eso*-oxy-αα-di-phenyl-propionic acid $C_{15}H_{12}Br_2O_4$. *Di-bromo-di-phenopropionic acid.* Formed by bromination of di-pheno-propionic acid $CH_3.C(C_6H_4OH)_2.CO_2H$. Amorphous powder. Sol. alcohol, insol. water.

Di-acetyl derivative $C_{15}H_{10}Br_2(OAc)_2O_2$; insoluble light yellow powder (Böttinger, *B.* 16, 2073).

Tri-bromo-*p*-oxy-phenyl-propionic acid $C_6H_3Br(OH).CHBr.CHBr.CO_2H$. *Bromo-p-coumaric-acid-di-bromide.* [188°]. Obtained by the action of bromine upon *p*-coumaric acid. Needles. By alcoholic KOH it is converted into tri-bromo-oxy-ethyl-benzene $C_6H_3Br(OH).CHBr.CH_2Br$.

Methyl derivative $C_6H_3Br(OMe).CHBr.CHBr.CO_2H$: [162°]; needles. Formed by the action of bromine upon the methyl derivative of *p*-coumaric acid $C_6H_4(OMe).CH:CH.CO_2H$. By heating with aqueous KOH (30 p.c.) it is converted into bromo-methoxy-phenyl-acetylene $C_6H_3Br(OMe).C:CH$ (Eigel, *B.* 20, 2534).

o-α-β-tri-bromo-*o*-oxy-phenyl-propionic acid *Methyl derivative* $C_6H_3Br(OMe)CHBr.CHBr.CO_2H$. [185°–188°]. S. (chloroform) ·42. From methyl-*o*-coumaric acid and bromine vapour (Perkin, *C. J.* 39, 417). White nodules (from benzene).

Boiled with sodium acetate it gives off CO_2 forming the methyl derivative of *o-exo*-dibromo-*o*-vinyl-phenol, $C_6H_3Br(OMe)C_2H_2Br$, a viscid oil. Strong KOH (1:1) gives the methyl derivative of bromo-oxy-phenyl-propiolic acid (*q.v.*).

Tetra-bromo-*o*-oxy-phenyl-propionic acid *Methyl derivative* $C_6H_2Br_2(OMe).CHBr.CHBr.CO_2H$. [202°]. From the preceding and Br (P.).

DI-BROMO-DI-OXY-DI-PHENYL SULPHIDE. $S(C_6H_3Br.OH)_2$. [173°]. From *p*-bromo-phenol and SCl_2 in CS_2 (Tassinari, *G.* 17, 91). Amorphous, reduced by zinc-dust to $S(C_6H_4OH)_2$. [128°].

DI-BROMO-DI-OXY-DI-PHENYL-SULPHONE. *Di-methyl derivative* $SO_2(C_6H_3(OMe)Br)_2$. [166°]. From $SO_2(C_6H_4.OMe)_2$ and Br. Small plates, v. sol. boiling alcohol (Annaheim, *A.* 172, 48).

Di-ethyl-derivative $SO_2(C_6H_3(OEt)Br)_2$. [183°].

Di-isoamyl derivative $SO_2(C_6H_3(OC_5H_{11})Br)_2$. [100°].

Tetra-bromo-di-oxy-di-phenyl sulphone $SO_2(C_6H_2Br_2.OH)_2$. [279°]. From di-oxy-di-phenyl-sulphone and Br. Thick monoclinic prisms (from alcohol).

TETRA-BROMO-OXY-PHENYL-VALERIC ACID. *Methyl derivative* $C_6H_2Br_2(OMe)CHBr.CEtBr.CO_2H$. [159°]. From (α) and (β) methoxy-phenyl-angelic acids and bromine vapour. Crystallised from light petroleum (Perkin, *C. J.* 39, 437).

Di-bromo-di-oxy-phenyl-valeric acid *Methylene derivative* $C_{12}H_{12}Br_2O_4$ *i.e.* $CH_2{<}^{O}_{O}{>}C_6H_3.C_4H_6Br_2.CO_2H$. *Di-bromo-piperhydronic acid.* [136°–140°]. From (α)-hydropiperic acid and Br (Fittig a. Mielck, *A.* 172, 159; Weinstein, *A.* 227, 33). Warm NaOHAq gives piperic acid. Sodium-amalgam gives hydropiperic acid.

Tetra-bromo-di-oxy-phenyl-valeric acid *Methylene derivative*

$$CH_2{<}^{O}_{O}{>}C_6H_3.CHBr.CHBr.CHBr.CHBr.CO_2H.$$

Tetra-bromo-piperhydronic acid. [160°–165°]. From piperic acid and Br (F. a. M.). Alkalis give HBr and piperonal $CH_2O_2.C_6H_3.CHO$. Boiling water produces HBr and '*di-bromo-piperinide*' $C_{12}H_8Br_2O_4$ [136°]; this body crystallises from alcohol in prisms, insol. water and alkalis, converted into piperonal by boiling aqueous Na_2CO_3. Further treatment with water converts di-bromo-piperinide into bromo-oxy-piperinide $C_{12}H_9BrO_5$ [132°], which separates from alcohol in monoclinic crystals, insol. aqueous Na_2CO_3.

BROMO-DI-OXY-PHTHALIDE. *Di-methyl derivative* $C_{10}H_9BrO_4$ *i.e.*

$$C_6H_3Br(OMe)_2{<}^{CO}_{CH_2}{>}O\ \left[x:6:5:{}^2_1\right].$$

Bromo-pseudo-meconine. [142°]. White flocculent solid (Salomon, *B.* 20, 887).

BROMO-OXY-PIPERINIDE *v.* TETRA-BROMO-DI-OXY-PHENYL-VALERIC ACID.

α-BROMO-β-OXY-PROPIONIC ACID $C_3H_5BrO_3$ *i.e.* $CH_2(OH).CHBr.CO_2H$. *Bromo-hydracrylic acid.* Formed by warming silver αβ-di-bromo-propionate with water (Beckurts a. Otto, *B.* 18, 236). Syrup; converted by moist Ag_2O into glyceric acid. *Salt.*—ZnA'_2.

β-Bromo-α-oxy-propionic acid $CH_2Br.CH(OH).CO_2H$. *β-Bromo-lactic acid.* [90°]. From oxy-acrylic acid and HBr (Melikoff, *B.* 13, 958). Prisms (from ether); miscible with water.

Di-ethyl ether $CH_2Br.CH(OEt).CO_2Et$. From $CH_2Br.CHBr.CO_2Et$ and NaOEt (Michael, *J. pr.* [2] 35, 136).

αβ-Di-bromo-α-oxy-propionic acid $CH_2Br.CBr(OH).CO_2H$. *Di-bromo-lactic acid.* [98°]. From acroleïn dibromide and cold dilute HNO_3 (Linnemann a. Penl, *B.* 8, 1101).

ββ-Di-bromo-α-oxy-propionic acid $CHBr_2.CH(OH).CO_2H$. *Di-bromo-lactic acid.* From the nitrile and HClAq. Syrup.

Nitrile $CHBr_2.CH(OH).CN$. From di-bromo-aldehyde and HCN. Oil (Pinner, *A.* 179, 71; *B.* 7, 1501).

βββ-Tri-bromo-oxy-propionic acid $CBr_3.CH(OH).CO_2H$. *Tri-bromo-lactic acid.* [143°]. From bromal, HCN, and HCl (Pinner, *B.* 7, 1501; Wallach, *A.* 193, 50).

Ethyl ether EtA' [46°]; prisms.

Nitrile $CBr_3.CH(OH).CN$. From bromal hydrate and conc. HCNAq. Prisms, v. sol. water.

Tri-bromo-ethylidene ether *v.* BROMALIDE.

Tri-chloro-ethylidene ether $CCl_3.CH(C_3HBr_3O_3)_2$. [134°]. Formed by heating the acid with chloral.

DI-BROMO-DI-OXY-PROPYL-BENZENE *v.* BROMO-EUGENOL.

Di-bromo-tri-oxy-propyl-benzene. *Di-bromo-propyl-pyrogallol.*

Di-methyl derivative $C_{11}H_{14}Br_2O_3$ *i.e.* $C_6(C_3H_7)Br_2(OH)(OMe)_2$. [109°]. *Acetyl derivative* $C_6(C_3H_7)Br_2(OAc)(OMe)_2$ [102°].

Methyl di-acetyl derivative $C_6(C_3H_7)Br_2(OAc)_2(OMe)$. [79°]. These compounds are formed by brominating the corresponding derivatives of tri-oxy-propyl-benzene (Hofmann, *B.* 11, 331; Brezina, *M.* 4, 492; Pastrovich, *M.* 4, 185).

DI-BROMO-DI-OXY-DI-PROPYL-MALONIC ACID $(CH_2Br.CH(OH).CH_2)_2C(CO_2H)_2$.

Di-lactone

$$\begin{array}{ccccc} CH_2Br.CH.CH_2 & \searrow & & \swarrow & CH_2.CH.CH_2Br \\ | & & C & & | \\ O.CO & \nearrow & & \nwarrow & CO.O \end{array} \quad [130°].$$

From di-allyl-malonic acid in glacial HOAc by Br (Hjelt, *B.* 15, 625; *A.* 216, 61). The tetrabromide $(CH_2Br.CHBr.CH_2)_2C(CO_2H)_2$ is first formed, but splits off 2HBr. Small plates (from alcohol). Insol. cold water, sl. sol. boiling water, v. sol. warm alcohol, sl. sol. ether. When boiled with baryta it ought to form $Ba(CO_2)_2C(CH_2.CH(OH).CH_2OH)_2$ but this splits off $BaCO_3$ forming the lactonic acid:

$$\begin{array}{ccc} CH_2OH.CH.CH_2 & \searrow & \\ | & & CH.CH_2.CH(OH).CH_2OH \\ O-CO & \nearrow & \end{array}$$

DI-BROMO-OXY-PYRIDINE $C_5H_3Br_2NO$ *i.e.* $C_5H_2Br_2(OH)N$. Prepared by heating piperidine with Br and water to 200° (Hofmann, *B.* 12, 984). Glistening scales. Sl. sol. water, ether, and alcohol. Sol. aqueous acids and alkalis.—$(B'HCl)_2PtCl_4$: long needles.—$C_5H_2AgBr_2ON$: white pp.

Methyl derivative: [193°]; long needles.

Di-bromo-oxy-pyridine $C_5H_2Br_2(OH)N$. [207°]. Long white needles. Formed by adding bromine-water to a solution of oxy-pyridine [107°] (Königs a. Geigy, *B.* 17, 591).

Di-bromo-oxy-pyridine $C_5H_2Br_2(OH)N$. [c. 200°]. Formed by the action of bromine-water upon (β)-oxy-pyridine [125°]. Colourless needles. V. sol. water and alcohol, nearly insol. benzene. Fe_2Cl_6 gives a violet colouration.

Salts.—$B'HBr$: small white silky needles. $B'_2H_2SO_4$*: easily soluble plates.—$B'_2H_2C_2O_4$*: needles sl. sol. alcohol. The picrate forms yellow needles (Fischer a. Renouf, *B.* 17, 1898).

BROMO-OXY-PYRIDINE-CARBOXYLIC ACID $C_5H_2N(Br)(OH)CO_2H$ [1:x:2:5]. *Bromo-oxy-nicotinic acid.* [296°]. Obtained by saponification of the methyl-ether, which is formed by the action of aqueous NH_3 upon the methyl-ether of bromo-cumalic acid. Sl. sol. hot water, nearly insol. ether, alcohol, and acetic acid.

Methyl ether $C_5H_2N(Br)(OH)CO_2Me$. [222°]. Slender glistening needles. Sol. hot water and hot alcohol.

Phenyl derivative of the *methyl-ether* $C_5H_2N(Br)(OPh)CO_2Me$. [183°]. Formed by the action of aniline on the methyl-ether of cumalic acid in alcoholic solution. Distils without decomposition; white glistening needles, sol. alcohol and ether, insol. water (Pechmann a. Welsh, *B.* 17, 2398).

DI-BROMO-OXY-QUINOLINE $C_9H_4Br_2(OH)N$. [195°]. Prepared by the action of bromine-water on a solution of oxy-quinoline (Bedall a. Fischer, *B.* 14, 1367). White silky needles. Sol. alcohol, ether, benzene, CS_2, insol. water, ligroïn, and dilute acids.

V. also BROMO-CARBOSTYRIL.

BROMO-(B. 4)-OXY-QUINOLINE TETRA-HYDRIDE. *Ethyl ether* $C_9H_8Br_2(OEt)N$. [45°]. Obtained by adding bromine to a cooled chloroform solution of (B. 4)-ethoxy-tetra-hydro-quinoline. Long triclinic crystals. The hydrochloride crystallises in felted needles, the sulphate in colourless plates, and the oxalate in prisms. The picrate forms sparingly soluble yellow needles [108°]. The nitrosamine forms glistening plates [86°] (Fischer a. Renouf, *B.* 17, 760).

DI-p-BROMO-DI-OXY-QUINONE $C_6Br_2(OH)_2O_2$ [1:4:2:5:3:6]. *Bromanilic acid.*

Formation.—1. By dissolving di-, tri-, or tetra-bromo-quinone in potash (Stenhouse, *A.* 91, 311; Sarauw, *A.* 209, 115).—2. By heating the sodium salt of di-oxy-quinone-di-*p*-carboxylic acid with conc. HBr.—3. Together with tetra-bromo-quinone by heating (1,3,5,2)-tri-bromo-phenol with pyrosulphuric acid at 115°; the reaction is anomalous as the two Br should remain *m* to one another (Salzmann, *B.* 20, 1997), *v.* also DI-CHLORO-DI-OXY-QUINONE.

Properties.—Monosymmetrical dark-red needles or bronzy plates. Converted by Br into hexa-bromo-acetone. A neutral solution of the Na salt gives the following reactions:—$CaCl_2$: brown pp.—$BaCl_2$: yellowish-brown pp.—$FeSO_4$ and $NiSO_4$: greenish-grey pp.—Fe_2Cl_6: brownish-black.—$Co(NO_3)_2$: brown.—$Pb(OAc)_2$: reddish-brown.—$CuSO_4$: greenish-brown.—$AgNO_3$ and $Hg_2(NO_3)_2$: red. $HgCl_2$: no pp.

Salts.—$Na_2A''4aq$: asymmetric crystals.—$K_2A''2aq$: asymmetric crystals.—$K_2A''aq$ (Hantzsch, *B.* 20, 1303; Hantzsch a. Schniter, *B.* 20, 2040, 2279).

Di-bromo-di-oxy-quinone. *Di-methyl derivative* $C_6Br_2(OMe)_2O_2$. [175°] (Hofmann, *B.* 11, 332).

Tri-bromo-oxy-quinone $C_6(OH)Br_3O_2$. [207°]. From oxy-hydroquinone and Br (Barth a. Schreder, *M.* 5, 593). Orange grains; sol. alcohol and $CHCl_3$.

DI-BROMO-OXY-TOLUIC ACID. *Methyl ether* $C_6HBr_2Me(OMe).CO_2H$ [?:?:4:2:1]. [194°]. From the methyl derivative of di-bromo-thymol by oxidation (Paternò a. Canzoneri, *G.* 10, 233).

DI-BROMO-OXY-TOLUQUINONE $C_6MeBr_2(OH)O_2$. [197°]. Formed in small quantity by the action of dilute KOH on tri-bromo-toluquinone (Spica a. Magnanimi, *G.* 13, 312).

BROMO-OXY-TOLYL-PHENYL-KETONE-CARBOXYLIC ACID $C_6H_4(CO_2H).CO.C_6H_2(CH_3)(Br)OH$. [228°]. Prepared by the action of Br and acetic acid on an alcoholic solution of *o*-cresol-phthaleïn. Small prisms. By heating with H_2SO_4 to 130° it is readily converted into bromo-oxy-methyl-anthraquinone. *Chloride* [208°] (Fraude, *B.* 12, 239).

DI-β-BROMO-OXY-α-TOLYL-PROPIONIC ACID $C_{10}H_{10}Br_2O_3$ *i.e.* $CHBr_2.C(C_7H_7)(OH).CO_2H$. *Di-bromo-eso-methyl-atrolactic acid.* [163°]. Prisms or needles. Prepared by dissolving di-bromo-pyruvic acid and toluene in H_2SO_4 at 0°. By hot water it is decomposed into CO_2 and tolyl bromo-methyl ketone $C_7H_7.CO.CH_2Br$. On reduction it gives *eso*-methyl-atrolactic acid (Böttinger, *B.* 14, 1597).

BROMO-OXY-VALERIC ACID. *Lactone.* $CH_3.\underline{CH.CHBr.CH_2.CO.O}$. From βγ-di-bromo-valeric acid by boiling with water (Messer-

schmidt, *A.* 208, 102). Non-volatile oil; converted by boiling baryta-water into di-oxy-valeric acid.

Di-bromo-oxy-valeric acid.

Lactone $CH_2Br.CBr.CH_2.CH_2.CO.O$ or $CH_3.CBr.CHBr.CH_2.CO.O$. [78°-81°]. From (α)-angelico-lactone and bromine. Thick white hygroscopic needles (from CS_2). Water converts it into HBr and bromo-levulic acid (Wolff, *A.* 229, 264).

DI-BROMO-PALMITIC ACID $C_{16}H_{30}Br_2O_2$. [29°]. From hypogæic acid and Br (Schröder, *A.* 143, 24). Amorphous and insol. water. Alcoholic KOH converts it into bromo-hypogæic and palmitolic acids. Aqueous alkalis form di-oxy-palmitic acid.

Di-bromo-palmitic acid $C_{16}H_{30}Br_2O_2$. From gaïolic acid and Br. Crystalline; converted by alcoholic KOH into palmitolic acid (S.).

Tri-bromo-palmitic acid $C_{16}H_{29}Br_3O_2$. [39°]. From bromo-hypogæic acid and Br. Amorphous (S.).

Tetra-bromo-palmitic acid. $C_{16}H_{28}Br_4O_2$. Yellow crystals.

BROMO-PALMITOLIC ACID $C_{16}H_{27}BrO_2$. [31°]. From tri-bromo-palmitic acid (*v. sup.*) and alcoholic KOH (S.).

BROMO-PENTANE *v.* AMYL BROMIDE.

αβ-Di-bromo-pentane $C_5H_{10}Br_2$ *i.e.* $CH_3.CH_2.CHBr.CHBr.CH_3$. *Amylene bromide.* (178°). S.G. $\frac{14}{0}$ 1·6868. From the corresponding amylene and Br (Wagner a. Saytzeff, *A.* 179, 307).

ωω-Di-bromo-isopentane $Pr.CH_2.CHBr_2$. *Isoamylidene bromide.* (170°-180°). From isovaleric aldehyde and PCl_3Br_2 (Bruylants, *B.* 8, 406). Alcoholic KOH gives PrCH:CHBr (111°) and Pr.C:CH.

αα-Di-bromo-pentane $Pr.CBr_2.CH_3$. From methyl propyl ketone and PCl_3Br_2 (B.). Split up by distillation into HBr and $Pr.CBr:CH_2$ (123°).

αβ-Di-bromo-isopentane $(CH_3)_2.CBr.CHBr.CH_3$. (170°-175°). S.G. $\frac{15}{1}$ 1·6370. M.M. 12·947 at 12·6°. From tri-methyl-ethylene and Br (Wurtz, *A. Ch.* [3] 35, 458; Bauer, *Bl.* 2, 149). Converted by water (20 vols.) and PbO at 150° into methyl isopropyl ketone (Eltekoff, *J. R.* 10, 215).

Isoamylene dibromide, formed by combination of Br with isoamylene from crude fusel oil, is a mixture of several of the preceding di-bromo-pentanes (Cahours, *C. R.* 31, 291; Wurtz, *A. Ch.* [3] 4, 458; *A.* 123, 202; Reboul, *C. R.* 58, 1058; *A.* 133, 84; Bauer, *Bl.* 1860, 148; *A.* 120, 167; *Z.* 1861, 590; Golowkinsky, *A.* 111, 252; Olevinsky, *Z.* 1861, 674).

Valerylene dihydrobromide (170°-175°), formed by the union of HBr with crude valerylene is also a mixture of di-bromo-pentanes.

Tri-bromo-pentane $C_5H_9Br_3$. From bromo-isoamylene and Br.

Tetra-bromo-pentane $C_5H_8Br_4$. *Valerylene tetrabromide.* [-10°]. From crude valerylene and Br (Reboul, *A.* 132, 119; 135, 372).

Tetra-bromo-pentane $C_5H_8Br_4$. *Piperylene tetrabromide.* [115°]. From piperylene and Br (Hofmann, *B.* 14, 664). A liquid isomeride is also formed (Magnanimi, *G.* 16, 390).

Tetra-bromo-pentane $C_5H_8Br_4$. *Isoprene tetra-bromide.* From isoprene (Tilden, *C. N.* 46, 120).

Penta-bromo-pentane $C_5H_7Br_5$. Two bodies of this composition are formed by the action of Br on valerylene in sunlight (R.).

BROMO-PENTENYL ALCOHOL *Ethyl ether* $C_7H_{13}BrO$ *i.e.* $C_5H_8Br.OEt$. (177°-180°). S.G. $\frac{19}{}$ 1·23. From tri-bromo-pentane and alcoholic KOH (Reboul, *A.* 133, 84).

BROMO-PENTINENE *v.* BROMO-VALERYLENE.

BROMO-PHENANTHRAQUINONE *v.* PHENANTHRAQUINONE.

BROMO-PHENANTHRENE *v.* PHENANTHRENE.

BROMO-DI-PHENIC ACID

$CO_2H.C_6H_4.C_6H_3Br.CO_2H$. [236° uncor.]. Formed, together with its di-bromide, by heating diphenic acid with bromine at 80°-100°. Small white prisms. Sublimes with difficulty. Not volatile with steam. V. sol. alcohol, ether, and acetic acid, sl. sol. benzene, chloroform and CS_2, insol. cold water.

Salts.—$A''Na_2$: white v. sol. amorphous powder.—$A''Ba$ 3aq: sparingly soluble needles.—$A''Ag_2$: white insol. pp.—$A''Cu$: sl. sol. amorphous green powder.

Di-ethyl ether $A''Et_2$: [65°]; crystals (Claus a. Erler, *B.* 19, 3149).

Bromo-di-phenic-acid-di-bromide

$C_{12}H_7Br_3(CO_2H)_2$. [256° uncor.]. Formed in small quantity (15 p.c.) by heating diphenic acid (1 mol.) with bromine (2 mols.) for 8 days at 100°. Glistening colourless needles (from hot alcohol). Sl. sol. ordinary solvents. Its alkaline solution decomposes very easily on heating, forming salts of di-bromo-di-phenic acid. It has a very bitter peculiar taste.—$A''Na$: soluble silky plates (Claus a. Edler, *B.* 19, 3152).

Bromo-di-phenic acid

[4:1] $C_6H_4(COOH).C_6H_3Br.COOH$ [1:4:2]. [208°]. Formed by oxidation of the liquid (1,4,1',4',2') mono-bromo-ditolyl with CrO_3 and acetic acid (Carnelley a. Thomson, *C. J.* 47, 590).

Di-bromo-di-phenic acid $C_{14}H_8Br_2O_4$. [296°]. From di-bromo-phenanthraquinone, $K_2Cr_2O_7$, and H_2SO_4. Geodes of small crystals, v. sl. sol. hot water, insol. alcohol and ether (Ostermayer, *B.* 7, 1091).

Di-bromo-di-phenic acid $C_{12}H_6Br_2(CO_2H)_2$. [245° uncor.]. Formed by heating di-phenic acid (1 mol.) with bromine (2 mols.) at 200°, or by heating aqueous solutions of salts of mono-bromo-di-phenic-acid-di-bromide. Small glistening needles. Not volatile with steam. Sublimes with difficulty. Sl. sol. benzene, chloroform, acetone, CS_2, and hot water, nearly insol. cold water, v. sol. alcohol, ether, and acetic acid.

Salts.—The alkaline salts are very soluble amorphous glassy masses. — $A''Ag_2$: white amorphous pp. — $A''Ca$ 3aq: easily soluble plates. —$A''Pb$: sl. sol. microcrystalline powder.

Di-ethyl ether $A''Et_2$: [106° uncor.] crystals (Claus a. Edler, *B.* 19, 3149).

o-BROMO-PHENOL C_6H_5BrO *i.e.* $C_6H_4Br(OH)$ [1:2]. (195°). From *o*-bromo-aniline by the diazo- reaction (Fittig a. Mager, *B.* 8, 362; Körner). Formed in small quantity in brominating phenol (Hübner a. Brenken, *B.* 6, 171). Oil; volatile with steam. Potash-fusion gives

resorcin. HNO_3 forms bromo-di-nitro-phenol [118°].

Methyl ether $C_6H_4Br.OMe$. (223°). From the methyl ether of *o*-amido-phenol by Sandmeyer's reaction (Wallach a. Hensler, *A.* 243, 238).

m-Bromo-phenol $C_6H_4Br(OH)$ [1:3]. [33°]. (236°). From *m*-bromo-aniline by the diazo-reaction (Körner, *G.* 4, 389; Wurster a. Nölting, *B.* 7, 905; F. a. M.). Crystalline. Potash-fusion gives resorcin. HNO_3 gives bromo-di-nitro-phenol [92°].

p-Bromo-phenol $C_6H_4Br(OH)$ [1:4]. [64°]. (237°). S.H. (18°–77°) ·3157. S. 1·422 at 15°.

Formation.—1. By distilling bromo-*o*-oxy-benzoic acid with $BaCO_3$ (Cahours, *A. Ch.* [3] 13, 102).—2. By passing air saturated with Br (160 pts.) into cooled phenol (94 pts.) (Körner, *A.* 137, 197).—3. Bromine (160g.) is dissolved in glacial HOAc (200 g.) and added to phenol (94 g.) dissolved in HOAc (300 g.) (Hübner a. Brenken, *B.* 6, 171).—4. From *p*-bromo-aniline by the diazo- reaction (K.; F. a. M.).

Properties.—Large crystals (from chloroform); sl. sol. water, v. sol. alcohol. Dimetric; $a:c = 1:1·46$. Its heat of neutralisation has been determined by Werner (*C. R.* 98, 1333; *Bl.* [2] 46, 281). Nitration gives bromo-di-nitro-phenol [76°]. Potash-fusion gives resorcin. SCl_2 forms $S(C_6H_3Br.OH)_2$ [176°] (Tassinari, *G.* 17, 83).

Methyl ether $C_6H_4Br.OMe$. *Bromo-anisol.* (223° cor.). S.G. $\frac{0}{0}$ 1·491.

Ethyl ether $C_6H_4Br.OEt$. (233°).

Isopropyl ether $C_6H_4Br.OPr$. (236°). S.G. $\frac{0}{0}$ 1·981. μ_D 1·553. From isopropyl phenol and Br (Silva, *Bl.* [2] 13, 27).

Benzoyl derivative $C_6H_4Br.OBz$. Crystalline.

Bromo-phenol (Fourth). (236°–238°) (Fittica, *J. pr.* [2] 28, 176; *B.* 19, 2632; *A. Ch.* [6] 4, 561).

Preparation.—Phenol (10 g.), alcohol (10 g.) and amorphous phosphorus (3 g.) are mixed and cooled while bromine (17 g.) is added through a capillary tube. The product is washed with dilute Na_2CO_3, dried and distilled. It contains di-bromo-phenol and the new body. This can only be distilled when in small quantities, in larger masses it undergoes carbonisation.

Properties.—Not solid at 10°.

Nitration.—Bromophenol (1 pt.), glacial acetic acid (3 pts.), and HNO_3 (S.G. 1·4) added gradually form crystals of a molecular compound $C_6H_3Br(NO_2)OH.C_6H_2Br(NO_2)_2OH$ which crystallises from alcohol and melts at [60°–65°]. Fuming HNO_3 converts this into a bromo-di-nitro-phenol [108°–110°], isomeric with those known. By the action of baryta on the above molecular compound a second such body $(C_6H_3Br(NO_2)OH)_2C_6H_2Br(NO_2)_2OH$ is got.

The existence of four bromo-phenols would be contrary to the general rule that only three isomeric di-derivatives of benzene can be obtained; according to Hand (*A.* 234, 129) the fourth bromo-phenol is merely *p*-bromo-phenol of which the melting-point is lowered by a trace of moisture.

Di-bromo-phenol $C_6H_3Br_2(OH)$ [1:3:4]. [40°]. S.H. (18°–73°) ·2436. S. ·194 at 15° (W.).

Formation.—1. By distilling di-bromo-salicylic acid with baryta (Cahours, *A.* 52, 329), or by heating with dilute H_2SO_4 at 280° (Peratoner, *G.* 16, 402).—2. By passing bromine-vapour (2 mols.) into cold phenol (1 mol.) (Körner, *A.* 137, 205).

Properties. — Crystalline mass, v. sl. sol. water, v. sol. ordinary solvents. HNO_3 forms picric acid. Its heat of neutralisation has been determined by Werner (*C. R.* 98, 1333). Heated with dilute H_2SO_4 in sealed tubes, it is converted into mono- and tri-bromo-phenol (Peratoner, *G.* 16, 403).

Methyl ether $C_6H_3Br_2(OMe)$. [59°]. (272°). From di-bromo-phenol, NaOH, and MeI. Formed also by brominating anisol (C.).

Nitro-benzoyl derivative $C_6H_3Br_2O.CO.C_6H_4NO_2$. [90°–100°]. From benzoyl-phenol by bromination followed by nitration.

Di-bromo-phenol $C_6H_3Br_2(OH)$ [6:2:1]. [56°]. Formed by distilling tetra-bromo-phenol-phthaleïn with conc. H_2SO_4 (Baeyer, *A.* 202, 138). Also from di-bromo-*p*-amido-phenol by displacing NH_2 by H (Möhlau, *B.* 15, 2494). Mass of thin needles (from water).

Di-bromo-phenol $C_6H_3Br_2(OH)$ [1:3:5]. [76·5°]. Formed, together with its methyl ether, by heating *s*-tri-bromo-benzene with NaOMe (Blau, *M.* 7, 621). Converted by potash-fusion into phloroglucin.

Methyl ether $C_6H_3Br_2(OMe)$: [38°].

Ethyl ether $C_6H_3Br_2(OEt)$. (268°). Formed by boiling di-bromo-*o*-di-azo-phenetol nitrate, $C_6H_2Br_2(OEt)N_2NO_3$, with water (Möhlau a. Oehmichen, *J. pr.* 132, 482).

Tri-bromo-phenol $C_6H_2Br_3(OH)$ [2:4:6:1]. [92°] (Wilsing, *A.* 215, 235); [95°] (Körner). S. ·007 at 15 (W.).

Formation.—1. From phenol and Br (Laurent, *A. Ch.* [3] 3, 211; Körner, *A.* 137, 208).—2. By distilling tri-bromo-salicylic acid with sand and baryta (C.).—3. By treating indigo with bromine-water.—4. From potassium phenol disulphonate and Br (Schmidt, *B.* 11, 852).

Properties.—Long silky needles (from dilute alcohol); may be sublimed. V. sl. sol. water, v. sol. alcohol. Its heat of neutralisation has been examined by Werner and Berthelot (*C. R.* 98, 1333; *A. Ch.* [6] 3, 552).

Reactions.—1. *Nitric acid* forms di-bromo-nitro-, bromo-di-nitro-, and tri-nitro-phenol (Armstrong a. Harrow, *C. J.* 29, 476).—2. CrO_3 and HOAc give tetra-bromo-quinone and amorphous insoluble $C_{12}H_4Br_6O_2$ (Benedikt, *A.* 199, 131).—3. *Bromine-water* forms $C_6H_2Br_3OBr$ (?) [118°] which forms yellow plates, insol. water, ether, and alcohol; it exhibits the following reactions: (*a*) At 130° it splits up into Br and the compound $C_{12}H_4Br_4O_2$. (*b*) Aniline forms tri-bromo-phenol and tri-bromo-aniline. (*c*) Phenol forms tri-bromo-phenol. (*d*) It is also reduced to tri-bromo-phenol by boiling alcohol or by Sn and HCl (Benedikt, *B.* 12, 1005; *M.* 1, 360; Werner, *Bl.* [2] 43, 373).

Ethyl ether $C_6H_2Br_3.OEt$. [69°]; prisms (Purgotti, *G.* 16, 526).

Propionyl derivative $C_3H_5O.O.C_6H_2Br_3$ [65°] (Guareschi a. Daccomo, *B.* 18, 1174).

Benzoyl derivative $C_6H_2Br_3OBz$: [82°]; small colourless prisms; soluble in alcohol and ether, nearly insol. water (Daccomo, *B.* 18, 1168).

Tri-bromo-phenol

Ethyl ether $C_6H_2Br_3.OEt$. [73°]. Prepared from tri-bromo-di-azo-phenetol by boiling with water and extracting the product with ether (Möhlau a. Oehmichen, *J. pr.* [2] 24, 484).

Tetra-bromo-phenol C_6HBr_4OH [2:3:4:6:1]. [120°]. From tri-bromo-phenol and Br at 180° (K.). Formed also by warming $C_6H_2Br_3OBr$ (*v. sup.*) with conc. H_2SO_4. Needles (from alcohol); may be sublimed. Bromine converts it into C_6HBr_4OBr [121°] which separates from chloroform in monoclinic crystals and is reduced by boiling alcohol or by Sn and HCl to tetra-bromo-phenol (Benedikt, *M.* 1, 361).

Penta-bromo-phenol $C_6Br_5.OH$. [225°]. Obtained by heating tri- or tetra- bromo-phenol with excess of Br at 220° for some days (Körner, *A.* 137, 210). Formed also by heating C_6HBr_4OBr with conc. H_2SO_4 (Benedikt, *M.* 1, 360). Adamantine needles (from CS_2); may be sublimed. Conc. HNO_3 forms bromopicrin and tetra-bromo-quinone. PBr_5 forms C_6Br_6 (Gessner, *B.* 9, 1505; Ruoff, *B.* 10, 1234).

Hexa-bromo-phenol C_6Br_5OBr. [128°]. Prepared by heating tri-bromo-phenol with excess of bromine in sealed tubes at 220°. Yellow crystals of trimetric system ($a:b:c = 1:.82:.114$); insol. cold alcohol, but decomposed by boiling into penta-bromo-phenol. On heating with aniline it yields penta-bromo-phenol and tri-bromo-aniline (Benedikt, *M.* 1, 363).

TETRA-BROMO-*p*-DIPHENOL *v.* TETRA-BROMO-DI-OXY-DIPHENYL.

TETRA-BROMO-PHENOL-PHTHALEÏN *v.* PHENOL-PHTHALEÏN.

BROMO-PHENOL *o*-SULPHONIC ACID $C_6H_3Br(OH).SO_3H$. The K salt is formed by adding Br (1 mol.) to an aqueous solution of potassium phenol *o*-sulphonate. The free acid is very deliquescent.—KA′: pointed needles—BaA'_2.—CuA'_2 (Senhofer, *A.* 156, 114).

Bromo-phenol *p*-sulphonic acid $C_6H_3Br(OH)(SO_3H)$ [2:1:4]. Formed as in the preceding case (S.), or by passing bromine-vapour into a cold conc. solution of phenol *p*-sulphonic acid (Le Canu, *C. R.* 103, 385). Deliquescent needles (containing 2aq).—KA′.

Bromo-phenol sulphonic acid.

Ethyl derivative $C_6H_3Br(OEt)(SO_3H)$. From potassium phenetol sulphonate and Br (Lippmann, *J.* 1870, 739). Deliquescent mass (containing 4aq).—KA′.

Bromo-phenol disulphonic acid $C_6H_2Br(OH)(SO_3H)_2$ [2:1:4:6]. From an aqueous solution of potassium phenol disulphonic acid (1 mol.) by adding Br (1 mol.) (Armstrong, *C. J.* 25, 865; Schmidt, *B.* 11, 852). Crystalline; v. sol. alcohol, m. sol. ether. Fe_2Cl_6 gives a red colour. HNO_3 forms bromo-nitro-phenol sulphonic acid, bromo-di-nitro-phenol, and tri-nitro-phenol.—BaA″ 2aq.—K_2A''.—PbA″.—Ag_2A''.

Di-bromo-phenol *o*-sulphonic acid $C_6H_2Br_2(OH)(SO_3H)$ [2:4:1:6]. [120°]. Formed by brominating potassium phenol *o*-sulphonate or bromo-phenol *o*-sulphonic acid (Armstrong, *C. J.* 25, 867; Senhofer, *A.* 156, 110; Schmidt, *B.* 11, 855). Concentric needles; deliquescent. The aqueous solution is coloured violet by Fe_2Cl_6 and is ppd. by $Pb(OAc)_2$.—HNO_3 forms di-bromo-*o*-nitro-phenol [117°]. $Ba(C_6H_2Br_2SO_4)_2$.— $BaC_6H_2Br_2SO_4$. — $CdC_6H_2Br_2SO_4$ 1½aq. — $KC_6H_3Br_2SO_4$.—$K_2C_6H_2Br_2SO_4$.—$PbC_6H_2Br_2SO_4$.

Di-bromo-phenol *p*-sulphonic acid $C_6H_2Br_2(OH)(SO_3H)$ [2:6:1:4]. From potassium phenol *p*-sulphonate (1 mol.) and Br (2 mols.) (Senhofer, *A.* 156, 103; Armstrong a. Brown, *C. J.* 25, 857); or by passing bromine-vapour into an aqueous solution of phenol *p*-sulphonic acid (Le Canu, *C. R.* 103, 385). Formed also by diazo- reaction from di-bromo-sulphanilic acid (Schmitt, *A.* 120, 161). Rectangular scales (containing aq). The solution is coloured violet by Fe_2Cl_6 but is not ppd. by $Pb(OAc)_2$.—

$KC_6H_3Br_2SO_4$ aq.—$K_2C_6H_2Br_2SO_4$ 2aq.—
$Ba(C_6H_3Br_2SO_4)_2$ 2aq.—$BaC_6H_2Br_2SO_4$ 4aq.

BROMO-PHENOXY-ACETIC ACID *v. Bromo-phenyl derivative* of GLYCOLLIC ACID.

BROMO-PHENOXY-PROPIONIC ACID *v. Bromo-phenyl derivative* of LACTIC ACID.

***o*-BROMO-DIPHENYL** $C_{12}H_9Br$ *i.e.* $C_6H_5.C_6H_4Br$ [1:2]. (298°). Formed by decomposing *o*-diazo-diphenyl perbromide with alcohol (Schultz, Schmidt, a. Strasser, *A.* 207, 353). Oil, smelling of oranges; oxidised by CrO_3 to *o*-bromo-benzoic acid.

***p*-Bromo-diphenyl** $C_6H_5.C_6H_4Br$ [1:4]. [89°] (310° i. V.). Formed by adding Br to a solution of diphenyl in CS_2. Laminæ; v. sol. hot alcohol and HOAc, v. e. sol. ether. Smells like oranges. Chromic acid oxidises it to *p*-bromo-benzoic acid (Schultz, *A.* 174, 207).

***pp*-Di-bromo-diphenyl** [4:1] $C_6H_4Br.C_6H_4Br$ [1:4]. [164°] (G.; F.); [162°] (C. a. T.). (c. 358°). Formed by heating diphenyl dissolved in CS_2 with bromine at 100° (Fittig, *A.* 132, 204; Carnelley a. Thomson, *C. J.* 47, 588). Also from benzidine by the diazo-reaction (Griess, *Pr.* 13, 383). Prisms and octahedra (C. a. T.); v. sl. sol. hot alcohol, slightly volatile with steam. Smells like oranges. Oxidised by CrO_3 to *p*-bromo-benzoic acid.

Tri-bromo-diphenyl [4:1] $C_6H_4Br.C_6H_3Br_2$. Formed by the action of bromine on a mixture of diphenyl and *p*-tolyl-benzene (Carnelley a. Thomson, *C. J.* 47, 587). Colourless silky needles, sl. sol. alcohol, not volatile with steam. CrO_3 in HOAc gives *p*-bromo-benzoic acid.

DI-BROMO-DI-PHENYL-ACETAMIDINE $C_{14}H_{12}Br_2N_2$ *i.e.* $CH_3.C(NHC_6H_4Br):NC_6H_4Br$. From *p*-bromo-aniline, HOAc, and PCl_3 (Dennstedt, *B.* 13, 233).—B′HCl.—$B'_2H_2PtCl_6$.

***o*-BROMO-PHENYL-ACETIC ACID** $C_8H_7BrO_2$ *i.e.* [2:1] $C_6H_4Br.CH_2.CO_2H$. [104°]. From phenyl-acetic acid, bromine and HgO. Separated from the *p*-compound by its more soluble barium salt (Bedson, *C. J.* 37, 95). Flat needles (from water). Monoclinic tablets (from glacial acetic acid).—$a:b:c = 1:.657:1.767$; $\alpha = 99°$ 44′. $KMnO_4$ oxidises it to *o*-bromo-benzoic acid.—CaA'_2.—AgA′.

Nitrile $C_6H_4Br.CH_2.CN$. Oil (Jackson a. White, *Am.* 2, 316).

***m*-Bromo-phenyl-acetic acid** [3:1] $C_6H_4Br.CH_2.CO_2H$. [97°] (J. a. W.); [100°] (G.). From (3, 4, 1)- bromo-amido-phenyl-acetic acid by removing NH_2 (Gabriel, *B.* 15, 841).

Nitrile $C_6H_4Br.CH_2.CN$. Oil (Jackson a. White, *P. Am. A.* 16, 256).

***p*-Bromo-phenyl-acetic acid** [4:1] $C_6H_4Br.CH_2.CO_2H$. [115°]. Prepared by treating phenyl-acetic acid with bromine and

HgO (Bedson, *C. J.* 37, 94).—Long flat needles; may be sublimed. Oxidation gives *p*-bromo-benzoic acid.

Salts.—AgA'.—NH_4A'. — BaA'_2. — CaA'_2.— CuA'_2.

Nitrile $C_6H_4Br.CH_2.CN$. [47°]. Prepared by boiling *p*-bromo-benzyl bromide with alcoholic KCN (Loring Jackson a. Lowery, *B.* 10, 1210; *Am.* 3, 248).

a-Bromo-phenyl-acetic acid $C_6H_5.CHBr.CO_2H$. [84°]. From mandelic acid and conc. HBrAq at 130° (Glaser a. Radziszowski, *Z.* 1868, 142). Formed also by brominating phenyl-acetic acid at 150° (Radziszewski, *B.* 2, 208). Monoclinic crystals (from CS_2). Reduced by sodium-amalgam to phenyl-acetic acid. Boiling NaOHAq gives mandelic acid $C_6H_5.CH(OH).CO_2H$. Alcoholic KOH gives $C_6H_5.CH(OEt).CO_2H$. The ethyl ether is converted by alcoholic KCy into $CO_2Et.CHPh.CHPh.CO_2Et$, and by Na into $CO_2Et.CPh:CPh.CO_2Et$.

Nitrile $C_6H_5.CHBr.CN$. Is the chief product of the action of bromine on benzyl cyanide at 120°. Sol. alcohol and ether. On heating to 170° or with alcoholic KCN it gives di-cyano-stilbene. With an excess of KCN di-cyano-dibenzyl is also formed. On boiling with alcoholic KOH it gives stilbene-di-carboxylic acid (Reimer, *B.* 14, 1797).

Hydrobromide of the Nitrile $C_6H_5.CHBr.CBr:NH$. *Phenyl-bromo-acetimido-bromide.* Formed together with the nitrile by the action of bromine on benzyl cyanide at 120°; the yield being 15 p.c. Colourless crystals. Bitter taste. Its vapour attacks the eyes. V. sl. sol. all solvents, most easily in boiling acetic acid. Decomposed by water and alcohol.—HCl at 150° converts it into *a*-bromo-phenyl-acetic acid (?) and NH_3. Dilute HCl at 150° converts it into NH_3, mandelic acid ($C_6H_5.CH(OH).CO_2H$), and HBr (Reimer, *B.* 14, 1797).

a-Bromo-di-phenyl-acetic acid $(C_6H_5)_2CBr.CO_2H$. From diphenyl-acetic acid and Br at 150°. Converted by boiling water into benzilic acid $CPh_2(OH).CO_2H$ (Symons a. Zincke, *A.* 171, 131).

Di-bromo-phenyl-acetic acid $C_6H_3Br_2.CH_2.CO_2H$. [115°]. Formed by action of sunlight on mixture of *o*- and *p*- bromo-phenyl-acetic acids and Br. Purified by conversion into the methyl ether, distillation and saponification (Bedson, *C. J.* 37, 96). White needles.—AgA'.

BROMO-PHENYL-ACRYLIC ACID *v.* BROMO-CINNAMIC ACID and BROMO-ATROPIC ACID.

DI-BROMO-DI-PHENYL-ALLOPHANIC ACID $C_{14}H_{10}N_2Br_2O_3$ *i.e.* $C_6H_4Br.NH.CO.N(C_6H_4Br).CO_2H$.

Ethyl ether. [153°]. The compound which is formed from *p*-bromophenyldicyanate by long boiling with alcohol is probably this ether. Fine white needles. Sol. alcohol and ether. By continued action of alcohol it is converted into *p*-bromo-phenyl-carbamic ether (Dennstedt, *B.* 13, 229).

***p*-BROMO-PHENYL-AMIDO-ACETIC ACID** $CH_2(NH.C_6H_4Br).CO_2H$. *Bromo-phenyl-glycocoll.* [98°]. Colourless crystals. V. e. sol. alcohol, ether and hot water. Forms a light-green copper salt. Prepared by the action of chloro-acetic acid on *p*-chloroaniline.

Ethyl ether A'Et: [96°]; white needles. Insol. water, sol. alcohol and ether.

p-Bromoanilide $CH_2(NH.C_6H_4Br).CONH(C_6H_4Br)$: [155°-160°]; white microscopic crystals. Sublimes at about 145°. Sl. sol. hot water, v. sol. alcohol and ether (Dennstedt, *B.* 13, 236).

Di-bromo-di-phenyl-amido-acetic acid. *Nitrile* $C_6H_3Br_2NH.CHPh.CN$. [92°]. From di-phenyl-amido-acetic acid and Br (Tiemann a. Piest, *B.* 15, 2032). Yellow rhombohedra (from alcohol).

Tri-bromo-phenyl-amido-acetic acid $C_6H_2Br_3.NH.CH_2.CO_2H$. Formed by adding bromine-water to an aqueous solution of phenyl-amido-acetic acid. Minute needles (from HOAc). Insol. water, acids and alkalis (Schwebel, *B.* 11, 1131).

BROMO-PHENYL-AMIDO-CHLORO-NAPHTHOQUINONE *v.* CHLORO-NAPHTHOQUINONE-BROMANILIDE.

a-BROMO-PHENYL-β-AMIDO-CROTONIC ACID $CH_3.C(NHPh):CBr.CO_2H$. *Anil-bromo-aceto-acetic acid.* [138°]. Formed by bromination of phenyl-β-amido-crotonic acid (anilacetacetic acid) dissolved in chloroform. Pearly plates, v. sol. hot alcohol, sl. sol. water, chloroform and ether. By cold H_2SO_4 it is condensed to (*Py.* 2:1:3)-bromo-oxy-methyl-quinoline (Knorr, *B.* 17, 2874).

BROMO-PHENYL-AMIDO-(a)-NAPHTHOQUINONE *v.* (a)-NAPHTHOQUINONE-BROMANILIDE.

TRI-BROMO-PHENYL-AMIDO-PROPIONITRILE $C_6H_2Br_3NH.CHMe.CN$. [130°]. From phenyl-*a*-amido-propionitrile and Br. Needles (Stephan, *C. C.* 1886, 470).

***p*-BROMO-PHENYL-(*Py.*3)-AMIDO-QUINOLINE** $C_6H_4\left\langle\begin{array}{l}CH:CH\\ \quad\ |\\ N:C(NH.C_6H_4.NO_2)\end{array}\right.$ [146°]. Silvery scales. Formed by heating (*Py.* 3)-chloro-quinoline with *p*-bromaniline (Friedländer a. Weinberg, *B.* 1[illegible], 1533).

DI-BROMO-DI-PHENYL-AMINE $HN(C_6H_4Br)_2$. [107°]. Prisms. Sol. alcohol and acetic acid. The benzoyl derivative is formed by bromination of benzoyl-di-phenyl-amine.

Benzoyl derivative $BzN(C_6H_4Br)_2$. [142°]. Colourless plates. Soluble in alcohol and acetic acid (Lellmann, *B.* 15, 830).

Tetra-bromo-di-phenyl-amine $NH(C_6H_3Br_2)_2$. [182°]. Formed by treating an alcoholic solution of di-phenyl-amine with Br. Needles (Hofmann, *A.* 132, 166; Gnehm, *B.* 8, 925).

Acetyl derivative $NAc(C_6H_3Br_2)_2$. [158°].

Hexa-bromo-di-phenyl-amine $NH(C_6H_2Br_3)_2$. [218°]. Formed, together with the preceding, by adding Br to a solution of di-phenyl-amine in HOAc (G.). Reduced by sodium-amalgam to di-phenyl-amine.

Octo-bromo-di-phenyl-amine $NH(C_6HBr_4)_2$. [c. 304°]. From di-phenyl-amine, Br, and I at 350°. Prisms (from $CHCl_3$) (Gessner, *B.* 9, 1511).

Deca-bromo-di-phenyl-amine $NH(C_6Br_5)_2$. From di-phenyl-amine, Br, and I at 350°. Needles (from $CHCl_3$). Not melted at 310°.

BROMO-PHENYL-BENZENE *v.* BROMO-DI-PHENYL.

Bromo-tri-phenyl-benzene $C_{24}H_{17}Br$. [104°]. From Br and tri-phenyl-benzene in CS_2. Needles (from alcohol) (Berthold a. Engler, *B.* 7, 1123).

BROMO-PHENYL-BENZOIC ACID v. BROMO-DIPHENYL-CARBOXYLIC ACID.

BROMO-PHENYL BENZYL OXIDE $C_6H_4Br.O.CH_2.C_6H_5$. [59°]. From phenyl benzyl oxide, Br, and HgO. Needles (Sintenis, *A.* 161, 335).

DI-*p*-BROMO-DI-PHENYL-BIURET $C_{14}H_{11}O_2Br_2N_3$ *i.e.* $(C_6H_4BrNH.CO)_2NH$. Prepared by the action of alcoholic NH_3 on *p*-bromo-phenyl-dicyanate (Dennstedt, *B.* 13, 230). Sl. sol. alcohol and ether, insol. water. Begins to sublime at about 240°.

γ-BROMO-γ-PHENYL-BUTYRIC ACID $Ph.CHBr.CH_2.CH_2.CO_2H$. [69°]. From γ-phenyl-iso-crotonic acid and conc. HBr at 0°. Crystals (from CS_2) (Jayne, *A.* 216, 102). By boiling with water or treatment with aqueous Na_2CO_3 it is converted into the lactone of γ-oxy-γ-phenyl-butyric acid (*q. v.*).

βγ-Di-bromo-γ-phenyl-butyric acid $Ph.CHBr.CHBr.CH_2.CO_2H$. [138°]. From phenyl-iso-crotonic acid in CS_2 by Br at 0° (Jayne, *A.* 216, 107). Crusts of small white crystals. Sodium amalgam converts it into sodium γ-oxy-γ-phenyl-butyrate.

exo-**Di-bromo-β-phenyl-isobutyric acid** $C_6H_5.CHBr.CBrMe.CO_2H$(?) [135°]. From phenyl-methacrylic acid and Br (Conrad a. Hodgkinson, *A.* 193, 312).

***p*-BROMO-PHENYL-CARBAMIC ACID**

Methyl ether $C_6H_4Br.NH.CO_2Me$. [124°]. From *p*-bromo-phenyl cyanate and MeOH. Needles (Dennstedt, *B.* 13, 229).

Ethyl ether $C_6H_4Br.NH.CO_2Et$. *Bromo-carbanilic ether.* [81°] (B.); [85°] (D.). From $PhNH.CO_2Et$ and bromine-water (Behrend, *A.* 233, 7) or from *p*-bromo-aniline and $ClCO_2Et$. Needles (from benzoline). Boiling alcoholic KOH gives K_2CO_3 and *p*-bromo-aniline.

Di-bromo-phenyl-carbamic acid. *Methyl ether* [4:2:1] $C_6H_3Br_2.NH.CO_2Me$. [97°]. Formed by brominating methyl phenyl-carbamate (Hentschel, *J. pr.* [2] 34, 423). Needles (from alcohol). Warm H_2SO_4 gives CO_2 and di-bromo-aniline.

Hexa-bromo-di-phenyl-carbamic ether $(C_6H_2Br_3)_2N.CO_2Et$. *Hexa-bromo-di-phenyl-amine urethane.* [184°]. Formed by bromination of di-phenyl-carbamic ether dissolved in acetic acid (Hager, *B.* 18, 2577). Long greenish-brown needles. Sol. acetic acid, nearly insol. alcohol.

***p*-BROMO-PHENYL-CARBAMINE DI-CHLORIDE** $C_6H_4Br.NCl:CCl$. (256°). From *p*-bromo-phenyl carbimide and Cl. Yellowish liquid (Dennstedt, *B.* 13, 232).

DI-BROMO-DI-PHENYL-CARBINOL $C_{13}H_{10}Br_2O$. [163°]. *Di-bromo-benzhydrol.* From di-phenyl-carbinol and Br. Minute needles (from alcohol). Reduced by sodium-amalgam to di-phenyl-carbinol (Linnemann, *A.* 133, 6).

DI-BROMO-PHENYL CARBONATE $(C_6H_3Br_2)_2CO_3$. [166°]. Silky needles; formed by brominating phenyl carbonate (Löwenberg, *C. C.* 1886, 390).

BROMO-DIPHENYL CARBOXYLIC ACID. [4:1] $C_6H_4Br.C_6H_4.CO_2H$ [1:4]. [194°]. From *p*-bromo-phenyl-toluene [30°] and CrO_3 in HOAc (Carnelley a. Thomson, *C. J.* 51, 88). V. sol. ether, sl. sol. alcohol.

Di-bromo-diphenyl carboxylic acid $C_{12}H_7Br_2.CO_2H$ [4′:1′:1:2or3:4]. *Di-bromo-phenyl-benzoic acid.* [204°]. From di-bromo-*p*-tolyl-benzene [115°] by oxidising with CrO_3 in HOAc. Needle-shaped prisms (from alcohol), sl. sol. alcohol (Carnelley a. Thomson, *C. J.* 47, 589).

Di-bromo-diphenyl *p*-carboxylic acid $C_6H_4Br.C_6H_3Br.CO_2H$ [4′:1′:1:2or3:4]. [232°]. Formed by oxidising di-bromo-tolyl-benzene [150°] (C. a. T., *C. J.* 51, 90).

Di-bromo-diphenyl carboxylic acid [212°] has been obtained from (β)-di-bromo-fluorene-ketone [197°] by potash-fusion (Holm, *B.* 16, 1081).—BaA'_2.

***p*-BROMO-PHENYL CYANATE** $OC:N.C_6H_4Br$ [1:4]. [39°]. (226°). V. sol. ether. Prepared by distilling bromo-phenyl-carbamic ether with P_2O_5 (Dennstedt, *B.* 13, 228).

***p*-BROMO-PHENYL DI-CYANATE** $C_{14}H_8N_2O_2Br_2$. [199°]. Small plates. Sl. sol. ether. Prepared by the action of a small quantity of tri-ethyl-phosphine on bromo-phenyl-cyanate heated to 100°. By long boiling with absolute alcohol it gives an acid of melting-point [153°] and formula $C_{16}H_{14}O_3N_2Br_2$ which is probably ethyl di-bromo-phenyl-allophanate (Dennstedt, *B.* 13, 229).

BROMO-PHENYL-CYSTEÏNE $C_9H_{10}BrNSO_2$ *i.e.* $C_6H_4Br.S.CMe(NH_2).CO_2H$. *p-Bromo-a-amido-thio-lactic acid.* [181°]. Formed by boiling bromo-phenyl-mercapturic acid with conc. HCl. Needles (from dilute alcohol); v. sl. sol. water, v. sl. sol. alcohol, v. sol. dilute HCl. Boiling alkalis slowly separate *p*-bromo-phenyl mercaptan and form pyruvic acid. Sodium-amalgam forms NH_3, lactic acid, and $C_6H_4Br.SH$. Acetic anhydride on warming gives an anhydride $C_6H_4Br.S.CMe\langle{NH \atop CO}\rangle$ [153°] 'bromo-phenyl-cystoïn,' but in presence of benzene it forms bromo-phenyl-mercapturic acid $C_6H_4Br.S.CMe(NHAc).CO_2H$. Potassium cyanate forms $C_6H_4Br.S.CMe(NH.CO.NH_2)CO_2H$.

Salts. — CuA'_2. — $HA'HCl$ (Baumann a. Preusse, *H.* 5, 315; *B.* 18, 258).

BROMO-*o*-PHENYLENE-DIAMINE $C_6H_3Br(NH_2)_2$ [4:1:2]. [63°]. From (1,3,4)- or (6,3,4)-bromo-nitro-aniline, tin, and HCl (Hübner, *A.* 210, 359; Wurster, *B.* 6, 1544; Remmers, *B.* 7, 347). Needles; v. sol. water. Sodium-amalgam reduces it to *o*-phenylene diamine.

Salts.—$B''HCl$.—$B''H_2SO_4$.

Di-bromo-*m*-phenylene-diamine $C_6H_2Br_2(NH_2)_2$. Dark brown pp. formed by adding bromine-water to an aqueous solution of *p*-phenylene-diamine hydrochloride; may be crystallised from alcohol (Hollemann, *Z.* 1865, 555).

BROMO-DIPHENYLENE KETONE $C_{13}H_7BrO$ *i.e.* $\left.\begin{array}{l} C_6H_4 \\ | \\ C_6H_3Br \end{array}\right\rangle CO$. [104°]. From bromo-fluorene and CrO_3 (Hodgkinson a. Matthews, *C. J.* 43, 165). Dark yellow needles.

Bromo-diphenylene ketone $C_{13}H_7BrO$. [122° uncor.]. Formed by distilling bromo-diphenic acid with lime. Yellow plates. V. sol. benzene, ether, and hot alcohol, nearly insol. water. Sublimes readily in felted needles. By distillation with zinc-dust it gives fluorene (Claus a. Erler, *B.* 19, 3155).

(α)-Di-bromo-diphenylene-ketone $C_{12}H_6Br_2CO$. [143°]. Formed by oxidation of di-bromo-fluorene [166°] with CrO_3 dissolved in acetic acid (Holm, *B.* 16, 1081). Long yellow needles. V. sol. ether and benzene.

(β)-Di-bromo-diphenylene ketone $C_{12}H_6Br_2CO$. [198°]. From (α) - di - bromo-fluorene [165°] by CrO_3 in slight excess and HOAc (Hodgkinson a. Matthews, *C. J.* 43, 165; Holm). Yellow needles, sol. alcohol, ether, and benzene. Potash-fusion gives rise to di-bromo-diphenyl-carboxylic acid.

Di-bromo-diphenylene-ketone $C_{12}H_6Br_2CO$. [133° uncor.]. Formed by distilling di-bromo-di-phenic acid with lime. Thin yellow plates or long thin needles. Readily sublimable (Claus a. Erler, *B.* 19, 3156).

DI - BROMO - DI - PHENYLENE KETONE OXIDE $C_{13}H_6Br_2O_2$ [210°–213°]. From di-phenylene ketone oxide and bromine at 180° (A. G. Perkin, *C. J.* 43, 193). Long needles (from alcohol). Combines with bromine forming an unstable addition product.

BROMO - DIPHENYLENE - METHANE *v.* BROMO-FLUORENE.

DI - BROMO - PHENYLENE-(α)-NAPHTHYL-ENE-OXIDE $C_{16}H_8Br_2O$. [284°]. Yellowish white needles. Sl. sol. benzene. Prepared by bromination of phenylene-(α)-naphthylene-oxide (Arx, *B.* 13, 1727).

BROMO-PHENYLENE OXIDE C_6H_3BrO. [195°]. From phenylene oxide and Br at 100°. Needles (from alcohol) (Märker, *A.* 124, 250).

Di-bromo-diphenylene oxide $C_{12}H_6Br_2O$. [185°]. From Br and diphenylene oxide in CS_2. Laminæ (from alcohol) (Hoffmeister, *A.* 159, 211).

DI - BROMO - DIPHENYLENE - PHENYL - METHANE $C_{19}H_{12}Br_2$. [182°]. From Br and the hydrocarbon in HOAc (Behr, *B.* 5, 971).

Tri-bromo-diphenylene-phenyl-methane $C_{19}H_{11}Br_3$ [167°–171°] (B.).

BROMO-PHENYL-ETHANE *v.* BROMO-ETHYL-BENZENE.

***p*-Bromo - di - phenyl - ethane** $C_{14}H_{13}Br$ *i.e.* $C_6H_5.CH_2.CH_2.C_6H_4Br$ [1:4]. *Bromo - dibenzyl.* S.G. 21·40. From *s*-di-phenyl-ethane, Br, and water (Fittig a. Stelling, *A.* 137, 266). Oil; boils above 320°.

***pp*-Di-bromo-di-phenyl-ethane** $C_{14}H_{12}Br_2$ *i.e.* [4:1] $C_6H_4Br.CH_2.CH_2.C_6H_4Br$ [1:4]. [115°]. From *s*-di-phenyl-ethane, water, and Br (F. a. S.). Needles (from alcohol). CrO_3 gives *p*-bromo-benzoic acid.

Exo-di-bromo-*s*-di-phenyl-ethane $C_6H_5CHBr.CHBr.C_6H_5$. [237°] (Z.); [235°] (K.). *Stilbene dibromide. Di-bromo-dibenzyl.*

Formation.—1. From stilbene and Br (Limpricht a. Schwanert, *A.* 145, 336).—2. From dibenzyl and dry Br (Marquardt, *A.* 151, 364).—3. From hydrobenzoïn and PBr_5 (Zincke, *A.* 198, 127).

Properties.—Silky needles. Decomposes at 235° (Kade, *J. pr.* 127, 465). V. sl. sol. boiling alcohol, m. sol. boiling xylene. Alcoholic KOH gives $C_6H_5.CH:CBr.C_6H_5$ and $C_6H_5.C:C.C_6H_5$. Converted by benzene and Al_2Cl_6 into *s*-tetra-phenyl-ethane some tri-phenyl-methane being also formed (Anschütz, *A.* 235, 207).

Tri - bromo - *s* - di - phenyl - ethane $C_{14}H_{11}Br_3$. From *s*-di-phenyl-ethane, water, and Br (F. a. S.). Nacreous laminæ, v. sl. sol. alcohol; decomposes at 170°.

Tri - bromo - *s* - di - phenyl - ethane $C_{14}H_{11}Br_3$ [207°–211°]. From *s*-di-phenyl-ethane and dry Br (M.).

Tri-bromo-*s*-di-phenyl-ethane $C_6H_5.CBr_2.CHBr.C_6H_5$. *Bromo-stilbene dibromide.* [100°]. From bromo-*s*-diphenyl-ethylene and Br (L. a. S.). Needles (from alcohol). Decomposed by distillation into HBr, PhCBr:CBr.Ph, and PhC:CPh. Alcoholic KOH gives PhC:CPh.

Tri-bromo-*u*-di-phenyl-ethane $(C_6H_5)_2CH.CBr_3$. [89°]. From bromal (1 mol.), benzene (2 mols.) and conc. H_2SO_4 (Goldschmiedt, *B.* 6, 985). Monoclinic prisms (from ether). Alcoholic KOH gives HBr and di-bromo-di-phenyl-ethylene.

Hexa - bromo-*s*-di - phenyl-ethylene $C_{14}H_8Br_6$. From *s*-di-phenyl-ethane and excess of Br. Hard prisms (from benzene) (F. a. S.).

BROMO-PHENYL-ETHYL-AMINE *v.* BROMO-AMIDO-PHENYL-ETHANE.

BROMO-*u*-DI-PHENYL-ETHYLENE $C_{14}H_{11}Br$ *i.e.* $(C_6H_5)_2C:CHBr$. [50°] (H.); [40°] (A.). (c. 170°) at 11 mm. (A.); (above 300°) (H.). Formed by warming the di-bromide of *u*-di-phenyl ethylene (Hepp, *B.* 7, 1410; Anschütz, *A.* 235, 160). Prisms; sl. sol. cold alcohol.

Bromo-*s*-di-phenyl-ethylene $C_6H_5.CBr:CH.C_6H_5$. *Bromo - stilbene.* [25°]. From stilbene di-bromide by distillation or treatment with alcoholic KOH. Prisms. AgOAc gives PhC(OAc):CHPh (Limpricht a. Schwanert, *A.* 145, 340; 155, 72).

Di-bromo-*u*-di-phenyl-ethylene $(C_6H_5)_2C:CBr_2$. [83°]. (above 300°). From $CPh_2H.CBr_3$ and alcoholic KOH (Goldschmiedt, *B.* 6, 985). Needles (from alcohol-ether).

Di-bromo-*s*-di-phenyl-ethylene $C_6H_5.CBr:CBr.C_6H_5$. *Tolane di-bromide.* [208°]. Leaflets. Prepared by the action of bromine on tolane. An isomeride [64°] is also formed in small quantity (Limpricht a. Schwanert, *A.* 145, 348; Liebermann a. Homeyer, *B.* 12, 1971). Converted by benzene and Al_2Cl_6 in presence of CS_2 into *s*-tetra-phenyl-ethane (Anschütz, *A.* 235, 209).

BROMO - PHENYL - GLYCOCOLL *v.* BROMO-PHENYL-AMIDO-ACETIC ACID.

DI-BROMO-DI-PHENYL-GUANIDINE $C_{13}H_{11}Br_2N_3$. From di-phenyl-guanidine hydrochloride, water, and Br (Hofmann, *A.* 67, 148). Scales (from alcohol).—B'HCl.—$B'_2H_2PtCl_6$.

Tri-bromo-tri-phenyl-guanidine $C_{19}H_{15}N_3Br_3Cl$ *i.e.* $(C_6H_4BrNH)_2C:N.C_6H_4Br$. White amorphous powder. Prepared by the action of *p*-bromaniline on iso-cyan-*p*-bromo-phenyl-chloride.—B'HCl: white crystals, easily soluble in alcohol and ether.—$(B'HCl)_2PtCl_4$: light yellow plates (Dennstedt, *B.* 13, 232).

***p*-BROMO-PHENYL-MERCAPTAN** $C_6H_4Br.SH$. [75°]. (231°). From *p*-bromo-benzene sulphochloride, tin, and HCl (Hübner a. Alsberg, *A.* 156, 327). Formed also by boiling bromo-phenyl-cysteïne or bromo-phenyl-mercapturic acid with NaOHAq (Baumann a. Preusse, *B.* 12, 806; *H.* 5, 319). Laminæ (from alcohol); volatile with steam; sl. sol. hot water. Conc. H_2SO_4 at 120° forms a green solution, turning blue. Sodium-amalgam forms phenyl-mercaptan. Chloral forms a compound

[72°]. HCl passed into a mixture of *p*-bromo-phenyl mercaptan and benzoic aldehyde forms di-*p*-bromo-di-phenyl-di-thio-benzaldehydate $C_6H_5.CH(S.C_6H_4Br)_2$ [80°] (Baumann, *B.* 18, 885). HCl and acetone form di-bromo-di-thio-di-methyl ketate $(CH_3)_2C(S.C_6H_4Br)_2$ [90°].

***p*-BROMO-PHENYL-MERCAPTURIC ACID** $C_{11}H_{10}BrNSO_3$ *i.e.* $C_6H_4BrS.CMe(NHAc).CO_2H$. *Acetyl-bromo-phenyl-amido-thio-lactic acid.* [153°]. S. 1·4 at 100°. Occurs in the urine of animals which have taken bromo-benzene. Formed also by treating bromo phenyl-cysteïne with benzene and Ac_2O (Baumann a. Preusse, *B.* 12, 806; *H.* 5, 309; Baumann, *B.* 15, 1732; Jaffe, *B.* 12, 1092). Needles; insol. cold water, sol. hot water and alcohol. Lævorotatory in alcoholic solution, dextrorotatory in alkaline solution. Boiling aqueous NaOH gives *p*-bromo-phenyl mercaptan, NH_3, HOAc, and pyruvic acid. Boiling conc. HClAq or dilute H_2SO_4 gives acetic acid and bromo-phenyl-cysteïne. Conc. H_2SO_4 gives a blue solution.

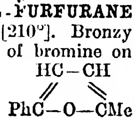
Salts.—BaA'_2 2aq: S. 2 at 15°.—MgA'_2 9aq. —NH_4A': S. 3 at 15°.

BROMO-DI-PHENYL-METHANE $C_{13}H_{11}Br$ *i.e.* $CHPh_2Br$. [45°]. From di-phenyl-methane (1 mol.) and Br (1 mol.) at 150° (Friedel a. Balsohn, *Bl.* [2] 33, 339, 587). Crystals, v. e. sol. benzene. Water at 100° forms di-phenyl-carbinol and its anhydride. Boiling alcohol forms $CHPh_2.OEt$. Conc. NH_3Aq gives $CHPh_2.NH_2$.

Di-bromo-di-phenyl-methane CPh_2Br_2. From di-phenyl-methane (1 mol.) and Br (2 mols.) at 150°. Liquid. Water at 150° converts it into benzophenone. Decomposed on distillation giving tetra-phenyl-ethylene. Sodium and water form tetra-phenyl-ethane.

Bromo-tri-phenyl-methane $C_{19}H_{15}Br$ *i.e.* Ph_3CBr. [152°]. Obtained by brominating tri-phenyl-methane in sunlight or at 150° (Allen a. Köllicker, *A.* 227, 107; Henderson, *C. J.* 51, 224; Schwarz, *B.* 14, 1520). Yellow hexagonal rhombohedra (from CS_2) $a:c = 1:·784$ (Hintze, *Z. K.* 9, 536). Decomposed above 200° into HBr and phenylene-di-phenyl-methane. Successive treatment with boiling HOAc and water forms tri-phenyl-carbinol. NH_3 forms Ph_3CNH_2. KCy gives $Ph_3C.Cy$. Potassium sulphocyanide gives $Ph_3C.SCN$.

TRI-BROMO-DI-PHENYL-METHYL-AMINE *v.* TRI-BROMO-METHYL-DI-PHENYL-AMINE.

BROMO-PHENYL-METHYL-FURFURANE TETRA-BROMIDE $C_{11}H_9Br_5O$. [210°]. Bronzy plates. Formed by the action of bromine on phenyl-methyl-furfurane  (Paal, *B.* 17, 2760).

BROMO-PHENYL-METHYL-PYRAZOLONE *v.* BROMO-OXY-PHENYL-METHYL-PYRAZOL.

γ-BROMO-γ-PHENYL-DI-METHYL-SUCCINIC ACID $Ph.CHBr.CH(CO_2H).CHMe.CO_2H$. From the lactone of γ-oxy-γ-phenyl-di-methyl-succinic acid (*q. v.*) and conc. HBr at 0° (Fittig a. Penfield, *A.* 216, 123). Small crystals (from benzene). V. sol. alcohol or ether, m. sol. benzene. Warmed with water it gives off CO_2 and forms plates of an acid which appears to be $Ph.CH:CH.CHMe.CO_2H$.

TETRA-BROMO-PHENYL-METHYL-THIOPHENE $C_{11}H_6Br_4S$. [187°]. Formed by bromination of phenyl-methyl-thiophene. Fine needles or plates. V. sol. benzene, ether, and petroleum-spirit, m. sol. alcohol and acetic acid (Paal a. Püschel, *B.* 20, 2559).

BROMO-PHENYL-METHYL-URETHANE *v.* *Methyl ether* of BROMO-PHENYL-CARBAMIC ACID.

BROMO-PHENYL MUSTARD OIL *v.* BROMO-PHENYL THIO-CARBIMIDE.

DI-BROMO-PHENYL-(β)-NAPHTHYL-AMINE $C_{16}H_{10}Br_2NH$. [140°]. White needles. Prepared by bromination of phenyl-(β)-naphthyl-amine (Streiff, *B.* 13, 1853; *A.* 209, 158).

Tetra-bromo-phenyl-(β)-naphthyl-amine $C_{16}H_8Br_4NH$. [198°]. Sl. sol. alcohol, ether and C_6H_6, m. sol. CS_2 and $CHCl_3$. Prepared by further bromination of the dibromo- derivative.

Tri-bromo-phenyl-(α)-naphthyl-amine $C_{16}H_9Br_3NH$. [137°]. Colourless prisms. Soluble in alcohol and benzene. Prepared by bromination of phenyl-(α)-naphthylamine (S.).

Tetra-bromo-phenyl-(β)-naphthyl-amine $C_{16}H_8Br_4NH$. [203°]. Formed by the action of bromine upon an acetic acid solution of benzene-azo-phenyl-(β)-naphthyl-amine, or by bromination of phenyl-(β)-naphthyl-amine. Long white silky needles (Zincke a. Lawson, *B.* 20, 1170).

BROMO-PHENYL-OCTANE *v.* BROMO-OCTYL-BENZENE.

***p*-BROMO-PHENYL-OXAMIC ACID** $C_6H_4Br.NH.CO.CO_2H$. [198°]. S. ·194 at 25°. From di-bromo-di-phenyl-oxamide and alcoholic KOH (Dyer a. Mixter, *Am.* 8, 355). Crystalline fibres, sol. alcohol and ether. KOHAq liberates *p*-bromo-aniline. Salts.—KA': monoclinic scales.—CaA'_2.—AgA'.—BaA'_2.

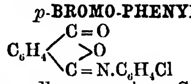
Ethyl ether EtA'. [156°]. From phenyl-oxamic ether and Br (Klinger, *A.* 184, 263).

DI-BROMO-DI-PHENYL-OXAMIDE $(C_6H_4Br.NH)_2C_2O_2$. [above 300°]. From Br and di-phenyl-oxamide in HOAc (D. a. M.)

DI-BROMO-DI-PHENYL OXIDE $(C_6H_4Br)_2O$. [58°]. (above 360°). From Br and di-phenyl oxide in CS_2. Long plates (from alcohol) (Merz a. Weith, *B.* 14, 191).

TRI-BROMO-TRI-PHENYL PHOSPHATE $(C_6H_4BrO)_3PO$. From tri-phenyl phosphate and Br at 180°. Nacreous scales (Glutz, *A.* 143, 193).

***p*-BROMO-PHENYL-PHTHALIMIDE**

 [204°]. Fine flat needles or scales. Sol. C_6H_6 and acetic acid, less in ether. Prepared by heating *p*-brom-aniline with phthalic anhydride (Gabriel, *B.* 11, 2261).

BROMO-PHENYL-PROPANE *v.* BROMO-PROPYL-BENZENE.

***o*-BROMO-β-PHENYL-PROPIONIC ACID** [2:1] $C_6H_4Br.C_2H_4.CO_2H$. *o-Bromo-hydrocinnamic acid.* [99°]. Scales. Formed by reduction of *o*-bromo-cinnamic acid with HI and P (Gabriel, *B.* 15, 2295).

***m*-Bromo-β-phenyl-propionic acid** [3:1] $C_6H_4Br.C_2H_4.CO_2H$. *m-Bromo-hydrocinnamic acid.* [75°]. Formed by reduction of *m*-bromo-cinnamic acid with P and HI. Also by eliminating the NH_2 group from (3:4:1)-bromo-amido-phenyl-propionic acid by diazotising and treatment with alcohol (Gabriel, *B.* 15, 2294).

Short thick prisms. V. sol. alcohol, ether, benzene, chloroform, and CS_2.

***p*-Bromo-β-phenyl-propionic acid** [4:1] $C_6H_4Br.CH_2.CH_2.CO_2H$. [135°]. From β-phenyl-propionic acid and Br in the cold (Göring, *C. C.* 1877, 793, 808; Gabriel a. Zimmermann, *B.* 13, 1683). Flat needles (from CS_2). Oxidation gives *p*-bromo-benzoic acid.

β-Bromo-β-phenyl-propionic acid $C_6H_5.CHBr.CH_2.CO_2H$. [137°]. From cinnamic acid and HBr (Fittig a. Binder, *B.* 10, 518; *A.* 195, 132; Anschütz a. Kinnicutt, *B.* 11, 1221). Also from β-bromo-β-oxy-phenyl propionic acid and HBr (Glaser, *A.* 147, 96). Laminæ. Decomposed by heat into HBr and cinnamic acid. Boiling water forms β-oxy-β-phenyl-propionic acid. Cold NaOHAq gives styrene and CO_2.

α-Bromo-α-phenyl-propionic acid $CH_3.CPhBr.CO_2H$. *Bromo-hydratropic acid.* [94°]. From atropic or atrolactic acids and cold conc. HBrAq (Fittig a. Wurster, *A.* 195, 145; Merling, *A.* 209, 13). Tables, insol. water, sol. ordinary solvents. Boiling Na_2CO_3Aq produces atrolactic acid.

β-Bromo-α-phenyl-propionic acid $CH_2Br.CHPh.CO_2H$. [94°]. Formed by heating atropic acid with conc. HBrAq at 100°. Prisms, insol. water. Boiling Na_2CO_3Aq produces tropic acid, styrene, and a very little atropic acid. Ammonia forms β-amido-α-phenyl-propionic acid [169°] (M.).

αβ-Di-bromo-β-phenyl-propionic acid $C_6H_5.CHBr.CHBr.CO_2H$. [195°] (G.); [201°] (S.). From cinnamic acid and bromine-vapour (Schmidt, *A.* 127, 320; Fittig a. Binder, *A.* 195, 140). Also from α-bromo-β-oxy-phenyl-propionic acid and HBr (Glaser, *A.* 147, 8?). Laminæ (from alcohol); v. sol. ether and alcohol, v. sl. sol. CS_2.

Reactions.—1. Sodium amalgam forms phenyl-propionic acid.—2. Boiling water gives cinnamic acid, bromo-oxy-phenyl-propionic acid, phenyl-acetic aldehyde and ω-bromo-styrene. 3. Alcoholic KOH gives α- and β- bromo-cinnamic acids.

Salts.—NaA'.—BaA'$_2$.

Methyl ether MeA'. [117°] (Anschütz, *B.* 12, 538).

Ethyl ether EtA' [69°]. From cinnamic ether and bromine (Perkin, jun., *C. J.* 45, 172).

n-Propyl ether PrA'. [23°].

αβ-Di-bromo-α-phenyl-propionic acid $CH_2Br.CPhBr.CO_2H$. [116°]. From Br and atropic acid in CS_2 (Fittig a. Wurster, *A.* 195, 145). Needles (from CS_2). Decomposed by boiling water into CO_2, HBr, and acetophenone. Sodium-amalgam forms α-phenyl-propionic acid and oxy-phenyl-propionic acid. Excess of NaOHAq gives atroglyceric acid $C_9H_{10}O_4$ (Fittig a. Kast, *A.* 206, 30).

Tri-bromo-phenyl-propionic acid $C_6H_5.CHBr.CBr_2.CO_2H$. [151°]. From bromo-cinnamic acid [120°] and Br (Glaser, *A.* 143, 335; Stockmeier, *Bn.* 2, 872; Kinnicutt, *Am.* 4, 25). Small flat monoclinic needles (from dilute alcohol). Boiling water gives CO_2, di-bromo-styrene, bromo-cinnamic acid, and di-bromo-oxy-phenyl-propionic acid.

Tri-bromo-phenyl-propionic acid $C_6H_5.CBr_2.CHBr.CO_2H$. [148°]. Formed by the combination of the bromo-cinnamic acid [159°] with Br. Triclinic prisms. Sol. hot benzene, v. e. sol. alcohol and ether, sl. sol. cold CS_2. It decomposes at its melting-point evolving HBr. By standing for a short time with water it is converted into a neutral oil; hot water decomposes it at once (Michael a. Brown, *B.* 19, 1380).

Tri-bromo-α-phenyl-propionic acid $C_9H_7Br_3O_2$. [150°]. From bromo-atropic acid and Br (F. a. W.). Needles (from ligroïn).

αβ-DI-BROMO-PHENYL-PROPIONIC ALDEHYDE $C_6H_5.CHBr.CHBr.CHO$. *Cinnamic aldehyde dibromide.* [c. 100°]. Small needles. Formed by the direct combination of cinnamic aldehyde and bromine. It readily splits off HBr on heating, giving bromo-cinnamic aldehyde (Zincke a. Hagen, *B.* 17, 1811).

DI-BROMO-β-PHENYL-PROPYL ALCOHOL $C_9H_{10}Br_2O$ *i.e.* $C_6H_5.CHBr.CHBr.CH_2OH$. *Styccrin dibromhydrin. Styrone dibromide.* [74°]. From Br and cinnamyl alcohol in $CHCl_3$ (Grimaux, *Bl.* [2] 20, 120). Tables or needles (from ether). Insol. water. Boiling water converts it into $C_6H_5.CH(OH).CH(OH).CH_2OH$.

Acetyl derivative $C_6H_5.CHBr.CHBr.CH_2OAc$: [86°]; prisms.

DI-BROMO-PHENYL-PROPYLIDENE-ANILINE $C_6H_5.N:CH.CHBr.CHBrPh$. [175°]. From cinnamylene-aniline and bromine (Schiff, *A.* 239, 384). Needles (from alcohol).

DI-BROMO-PHENYL-PYRAZOL DIHYDRIDE $C_9H_8Br_2N_2$. [93°]. *Di-bromo-phenyl-pyrazoline.* From phenyl-pyrazoline and Br in chloroform (Fischer a. Knoevenagel, *A.* 239, 199). Plates (from alcohol); v. sl. sol. water. In dilute acid solution it gives a violet colour with $K_2Cr_2O_7$. Alcoholic KOH forms $C_9H_8Br(OEt)N_2$ [66°], which crystallises from alcohol in pale yellow prisms. Boiling HClAq gives off EtCl and forms bromo-oxy-phenyl-pyrazol $C_9H_6Br(OH)N_2$ [214°]; this has acid characters and forms greenish-yellow crystals (from alcohol).

DI-BROMO-(α)-PHENYL-PYRIDINE DI-CARBOXYLIC ACID $C_{13}H_7Br_2NO_4$. [205°]. From [2:1] $C_6H_4(CO_2H).C_5H_3N(CO_2H)$ [3:2] and bromine (Skraup a. Cobenzil, *M.* 4, 469). Granules, v. sl. sol. water, m. sol. warm alcohol.

DI-BROMO-DI-PHENYL SULPHIDE $(C_6H_4Br)_2S$. [110°]. From di-phenyl sulphide and Br, or from $(C_6H_4NH_2)_2S$ by diazo-reaction. Nacreous laminæ (Krafft, *B.* 7, 1165).

Di-*p*-bromo-di-phenyl disulphide $(C_6H_4Br)_2S_2$. [94°]. From *p*-bromo-phenyl mercaptan by atmospheric oxidation. Plates; not volatile with steam (Hübner a. Alsberg, *A.* 156, 328; Baumann a. Preusse, *H.* 5, 329).

DI-*p*-BROMO-DI-PHENYL SULPHONE $(C_6H_4Br)_2SO_2$. [172°]. From *p*-bromo-benzene and $ClSO_3H$ (Armstrong, *C. J.* 24, 173) or SO_3 (Nölting, *B.* 8, 594). Also from bromo-benzene, benzene sulphochloride, and Al_2Cl_6 (Beckurts a. Otto, *B.* 11, 2065). Needles, sl. sol. hot alcohol.

***p*-BROMO-PHENYL-THIO-CARBAMIC ETHER** $C_9H_{10}BrNSO$ *i.e.* $C_6H_4Br.NH.CS.OEt$. *Bromo-phenyl-thio-urethane.* [105°]. From *p*-bromo-phenyl thio-carbimide and alcohol at 120° (Dennstedt, *B.* 13, 231). Slender needles.

***p*-Bromo-phenyl-di-thio-carbamic ether** $C_6H_4Br.NH.CS.SEt$. *Bromo-di-thio-carbanilic ether.* [89°]. From *p*-bromo-phenyl-thio-carbimide and mercaptan at 140° (D.).

p-Bromo-phenyl-thio-carbimide $C_6H_4Br.N.CS$. *p-Bromo-phenyl mustard oil.* [61°]. Prepared by heating *p*-bromo-aniline with CS_2 in alcoholic solution with a little aqueous KOH; the resulting thio-urea being distilled with P_2O_5 or heated with conc. HCl at 160° (Dennstedt, *B.* 13, 230; Weith and Landolt, *B.* 8, 716).

DI-p-BROMO-DI-PHENYL-DI-THIO-CINNAMIC ALDEHYDATE $C_6H_5.C_2H_2.CH(S.C_6H_4Br)_2$. *p-Bromo-phenyl-mercaptal of cinnamic aldehyde.* [107°]. Formed by passing HCl gas into a mixture of *p*-bromo-phenyl mercaptan and cinnamic aldehyde (Baumann, *B.* 18, 885). Long colourless needles. Sl. sol. cold alcohol and ether.

BROMO-PHENYL-THIO-GLYCOLLIC ACID $C_8H_7BrSO_2$ *i.e.* $C_6H_4Br.S.CH_2.CO_2H$. [112°]. From $C_6H_5S.CH_2.CO_2H$ and Br in CS_2 (Claësson, *Bl.* [2] 23, 441).

DI-p-BROMO-DI-PHENYL-DI-THIO-DI-METHYL-KETATE $(CH_3)_2:C:(SC_6H_4Br)_2$. *p-Bromo-phenyl-mercaptol of acetone.* [90°]. Long transparent prisms. V. sol. hot alcohol, ether, and benzene. Formed by passing HCl gas into a mixture of *p*-bromo-phenyl-mercaptan and acetone (Baumann, *B.* 18, 888).

p-BROMO-PHENYL-THIO-UREA $NH_2.CS.NHC_6H_4Br$. [183°]. From bromo-phenyl-thio-carbimide and alcoholic NH_3 (Dennstedt, *B.* 13, 231). Needles.

p-Bromo-di-phenyl-thio-urea $NHPh.CS.NH.C_6H_4Br$ [158°]. From bromo-phenyl-thio-carbimide and aniline (D.).

Di-p-bromo-di-phenyl-thio-urea $CS(NH.C_6H_4Br)_2$. [178°]. From *p*-bromo-aniline, CS_2, and alcohol in presence of some KOHAq (D.; Otto, *B.* 2, 409). Prisms.

BROMO-PHENYL-THIO-URETHANE *v.* BROMO-PHENYL-THIO-CARBAMIC ETHER.

TETRA-BROMO-PHENYL-p-TOLUIDINE $C_{13}H_9Br_4N$. [156°]. Formed by adding a solution of Br in glacial HOAc to an alcoholic solution of phenyl-*p*-toluidine (Bonna, *A.* 239, 58).

Hepta-bromo-phenyl-p-toluidine $C_{13}H_6Br_7N$. [185°]. From phenyl-*p*-toluidine and Br at 280°.

Endeca-bromo-phenyl-p-toluidine $C_{13}H_2Br_{11}N$. [296°]. Formed from phenyl-*p*-toluidine and Br at 310°.

BROMO-p-PHENYL-TOLUENE $C_{13}H_{11}Br$. [127°–131°]. From *p*-phenyl-toluene and Br. Small tables (from alcohol) (Carnelley a. Thomson, *C. J.* 47, 589).

DI-p-BROMO-DI-PHENYL-UREA $C_{13}H_{10}Br_2N_2O$ *i.e.* $CO(NH.C_6H_4Br)_2$. *Di-bromo-carbanilide.* From di-phenyl-thio-urea and Br (Otto, *B.* 2, 409). Formed also by decomposition of the product from $COCl_2$ and diazobenzene-*p*-bromanilide. Prepared by the action of carbonyl chloride on *p*-bromaniline (Sarauw, *B.* 15, 45). White glistening plates. Sublimes at 225° without melting. Sl. sol. alcohol and benzene.

Tetra-bromo-di-phenyl-urea $CO(NH.C_6H_3Br_2)_2$. Sublimes in needles (O).

BROMO-PHENYL-URETHANE *v.* BROMO-PHENYL-CARBAMIC ETHER.

DI-BROMO-PHENYL-VALERIC ACID $C_6H_5.CHBr.CHBr.CH_2.CH_2.CO_2H$. [109°]. From styryl-propionic acid and Br (Baeyer a. Jackson, *B.* 13, 122).

BROMO-PHLOBAPHENE *v.* PHLOBAPHENE.

BROMO-PHLORETIC ACID *v.* PHLORETIC ACID.

TRI-BROMO-PHLOROGLUCIN $C_6Br_3(OH)_3$. [151°]. Formed by brominating phloroglucin (Hlasiwetz, *A.* 96, 118; Herzig, *M.* 6, 885). Long needles (containing 3aq) (from water). Reduced by tin and HCl to phloroglucin. Converted by cold HNO_3 (S.G. 1·4) into tri-bromo-di-nitro-propionic acid (Benedikt, *A.* 184, 255).

Tri-acetyl derivative $C_6Br_3(OAc)_3$. [183°] (Herzig, *M.* 6, 887).

Hexa-bromo-phloroglucin dibromide $C_6Br_3(OBr)_3$. [118°]. The final product of the bromination of phloroglucin (Hazura a. Benedikt, *M.* 6, 702). Small golden needles (from $CHCl_3$). At 190° it gives off Br (1 mol.). Aqueous SO_2 reduces it to $C_6Br_3(OH)_3$. Tin and HCl form $C_6H_6Cl_3(OH)_3$.

DI-eso-BROMO-ν-PHOSPHO-AMIDO-BENZENE SULPHONIC ACID $(HO)_2PO.NH.C_6H_2Br_2.SO_3H$. The *chloride* $Cl_2PO.NH.C_6H_2Br_2.SO_2Cl$ is formed by treating di-bromo-amido-benzene sulphonic acid with PCl_5. It is converted by alcohol into the *ether-chloride* $(EtO)_2PO.NH.C_6H_2Br_2.SO_2Cl$ [c. 170°] (Laar, *J. pr.* [2] 20, 257).

BROMO-PHTHALACENE *v.* PHTHALACENE.

i-BROMO-PHTHALIC ACID $C_6H_3Br(CO_2H)_2$ [1:3:4]. [140°]. Formed, together with its isomeride, by brominating phthalic acid (Faust, *A.* 160, 62; Pechmann, *B.* 12, 2124; *cf.* Guareschi, *A.* 222, 295, Stallard, *C. J.* 49, 187). Powder, v. sol. water, alcohol, and ether.

Salts.—$K_2A''2aq$: long needles (from alcohol).—$BaA''2aq$: crystalline powder; sl. sol. water.—CuA''.—Ag_2A'': cheesy pp., sl. sol. water.

Anhydride $C_6H_3Br(CO)_2O$. [65°]. (300°–340°).

Ethyl ether Et_2A'': (295°); liquid.

c-Bromo-phthalic acid $C_6H_3Br(CO_2H)_2$ [1:2:3]. [176°] (G.); [174°] (M.); [197°] (C. a. T.).

Formation.—1. Together with the preceding, by brominating phthalic acid (Pechmann).—2. By the oxidation of bromo-nitro-naphthalene [122·5°] with $KMnO_4$ (Guareschi, *A.* 222, 292), of bromo-(β)-naphthol with $KMnO_4$ (Meldola, *C. J.* 47, 512), of liquid bromo-ditolyl (Carnelley a. Thomson, *C. J.* 47, 591), of di-bromo-naphthalene [130°] with CrO_3 in HOAc (Guareschi, *B.* 19, 134), of $C_{10}H_3Br_4(OH)$ [1:x:3:4:2] with $KMnO_4$ (Smith, *C. N.* 40, 87), and of (α)-bromo-naphthalene, and bromo-*o*-toluic acid [167°] with dilute HNO_3 (Racine, *A.* 239, 76). The bromo-*o*-toluic acid may be prepared from bromo-*o*-toluidine $C_6H_3MeBr(NH_2)$ [1:5:2]? by Sandmeyer's method; 70 g. of bromo-toluidine gave 53 g. of bromo-phthalic acid.

Properties.—White prisms (from water); v. sl. sol. chloroform, m. sol. water, alcohol, and ether. With resorcin it gives a fluoresceïn (Nourrisson, *B.* 20, 1016). The salt BaA'' forms pearly plates, sl. sol. water.

Anhydride $C_6H_3Br(CO)_2O$. [135°] (Meldola); [132°] (G.); [125°] (Smith); [108°] (Nourrisson); [95°] (Racine). Needles. Heated with phenol and H_2SO_4 it forms a body (? bromo-phthalide) that dissolves in alkalis forming a purple solution.

Di-bromo-phthalic acid $C_6H_2Br_2(CO_2H)_2$ [1:4:2:3]. [135°]. From di-bromo-naphthalene

[82°] and HNO_3. White crystalline powder, sol. boiling water and alcohol (Guareschi, *A.* 222, 274). On melting it changes to its anhydride.

Salt.—Na_2A''.

Anhydride [208°]. Pearly needles (by sublimation). Heated with phenol and H_2SO_4 it forms a product (dibromophthaleïn) that dissolves in potash forming a purple solution.

Di-bromo-phthalic acid $C_6H_2Br_2(CO_2H)_2$. [206°]. Formed by oxidation of penta-bromo-(α)-naphthol or of tetra-bromo-(α)-naphthoquinone by means of dilute HNO_3 at 150° (Blümlein, *B.* 17, 2490). Colourless needles. V. e. sol. alcohol, ether, and hot water.

Salts.—$A''Ag_2$: small colourless plates, sparingly soluble. $A''Ca$: pp.—$A''Ba$: pp.

Anhydride $C_6H_2Br_2<{CO \atop CO}>O$. [208°]. Sublimes in long colourless needles. Easily soluble in alcohol, sparingly in water and ether. Formed by heating the acid. Heated with resorcin it yields a di-bromo-fluoresceïn.

Di-bromo-tetra-hydro-phthalic acid $C_6H_6Br_2(CO_2H)_2$. *Di-bromo-tetra-hydro-benzene-di-o-carboxylic acid.* Formed by the direct combination of dry di-hydro-phthalic acid with bromine vapour. Rhombohedra (Baeyer, *B.* 19, 1810).

Tri-bromo-phthalic acid $C_6HBr_3(CO_2H)_2$. [191°]. Formed by oxidation of penta-bromo-(β)-naphthol or of tetra-bromo-(β)-naphthoquinone with HNO_3 (Flessa, *B.* 17, 1482). Small silvery plates or needles. Nearly insoluble in petroleum ether and in cold water.

Salts.—Ag_2A''.—CaA'' 2aq.—BaA'' 2aq.

Anhydride $C_6HBr_3(CO)_2O$: [157°]; sublimes in white plates; easily soluble in alcohol and ether, nearly insoluble in cold water.

Tetra-bromo-phthalic acid $C_6Br_4(CO_2H)_2$. [266°]. Formed by oxidation of tetra-bromo-o-xylene by heating with dilute HNO_3 and bromine at 170° (Blümlein, *B.* 17, 2493). Small needles or colourless prisms. V. sl. sol. water. With resorcin it yields a tetra-bromo-fluoresceïn.

Salts.—$A''Ca$.—$A''Ba$.

Anhydride $C_6Br_4<{CO \atop CO}>O$. [259°]. Formed by heating the acid. Sublimes in colourless glistening needles. Sl. sol. almost all solvents.

V. also BROMO-TEREPHTHALIC ACIDS.

BROMO-PHTHALIDE $C_6H_3Br<{CH_2 \atop CO}>O$. [3 or 6 : $\frac{1}{2}$]. [100°]. Formed in small quantity, together with bromo-o-toluic acid, by the action of bromine-water on o-toluic acid (Racine, *A.* 239, 76). Needles (from dilute alcohol); sublimes readily. Insol. cold water or Na_2CO_3Aq. Gives bromo-o-toluic acid [167°] on oxidation.

(α)-Bromo-phthalide $C_6H_4<{CHBr \atop CO}>O$. [86°]. From phthalide and bromine at 140° (Racine, *A.* 239, 79; *B.* 19, 778). Small cubes or tables (from ether). May be distilled. Hygroscopic. Slowly decomposed by cold, quickly by hot, water, forming phthalic aldehyde-acid $C_6H_4(CO_2H)(CHO)$. Alcohol converts it into $C_6H_4(CO_2Et)(CHO)$. $KMnO_4$ oxidises it to phthalic acid. Ammonia forms amido-phthalide, $C_6H_4<{CH(NH_2) \atop CO}>O$. [167°].

Di-bromo-phthalide $C_8H_4Br_2O_2$ *i.e.* $C_6H_2Br_2<{CH_2 \atop CO}>O$ $\left[{1 \; 2 \atop 4 \; 3}\right]$. [188°]. S. (94 p.c. alcohol) ·37 at 15°. From di-bromo-naphthalene, CrO_3 and glacial acetic acid (Guareschi, *A.* 222, 282). Prisms or needles (from alcohol). Neutral reaction. Does not reduce ammoniacal $AgNO_3$. With phenol and H_2SO_4 gives no dye on heating.

DI-BROMO-PICENE *v.* PICENE.

BROMO-PICRIN *v.* TRI-BROMO-NITRO-METHANE.

BROMO-PIPERHYDRONIC ACID *v.* BROMO-DI-OXY-PHENYL-VALERIC ACID.

BROMO-PIPERIC ACID *Dihydride.* $C_{12}H_{11}BrO_4$ or

$CH_2<{O \atop O}>C_6H_2Br.CH_2.CH_2CH:CH.CO_2H$.

Bromo-(β)-hydro-piperic acid. [171°]. From bromine and (β)-di-hydro-piperic acid (Fittig a. Buri, *A.* 216, 177; Weinstein, *A.* 227, 42). Streaky white plates (from benzene).—**Salt.**—CaA'_2.

Reactions.—1. Not affected by boiling aqueous KOH.—2. $KMnO_4$ oxidises it, in neutral solution, to bromo-piperonylic acid [204°], bromo-pipero-propionic acid (*q. v.*) and bromo-piperonal; hence Br is in the benzene nucleus.—3. *Sodium-amalgam* forms piperhydronic or methylene-di-oxy-phenyl-valeric acid $C_{12}H_{14}O_4$.

DI-BROMO-PIPERINIDE *v.* BROMO-TRI-OXY-PHENYL-VALERIC ACID.

BROMO-PIPERONYLIC ACID *v.* BROMO-DI-OXY-BENZOIC ACID.

BROMO-PIPERO-PROPIONIC ACID *v. Methylene derivative* of BROMO-DI-OXY-PHENYL-PROPIONIC ACID.

DI-BROMO-PREHNITOSE *v.* DI-BROMO-DURENE.

BROMO-PROPANE *v.* PROPYL BROMIDE.

Di-bromo-propane $C_3H_6Br_2$ *i.e.* $CH_3.CHBr.CH_2Br$. (141·5°). *Propylene bromide.* S.G. $\frac{0}{0}$ 1·9617 (Zander, *A.* 214, 175). S.V. 118·9 (Z.); 118·4 (Schiff).

Formation.—1. From propylene and Br (Reynolds, *A.* 77, 120; Cahours, *C. R.* 31, 291; Wurtz, *A.* 104, 244).—2. From bromo-propylene and HBr.—3. Together with trimethylene bromide by the union of HBr with allyl bromide (Geromont, *Bl.* [2] 16, 113, Reboul, *Bl.* [2] 17, 350). 4. From propyl bromide and Br (Linnemann, *A.* 161, 41).

Properties.—Liquid with sweet smell.

Reactions.—1. Alcoholic KOH forms two bromo-propylenes and, finally, allylene (Sawitsch, *C. R.* 52, 399).—2. AgOAc gives the di-acetyl derivative of propylene-glycol (Wurtz, *A. Ch.* [3] 4, 438). AgOBz gives the corresponding benzoyl derivative (Friedel a. Silva, *C. R.* 73, 1379).—3. Converted into propylene by Zn and HOAc or *sodium-amalgam* in alcohol (Linnemann, *B.* 10, 1111).—4. Aqueous HI at 150° gives isopropyl bromide.—5. Heated to 100° with Ag_2O and *water* it gives propionic aldehyde but no propylene-glycol (Beilstein a. Wiegand, *B.* 15, 1496).—6. *Water* (20 vols.) and PbO at 150° gives acetone, propionic aldehyde and propylene-glycol (Eltekoff, *J. R.* 10, 212).—7. Protracted boiling with *water* gives propylene-glycol (Niederist, *A.* 196, 349).

αα-Di-bromo-propane $CH_3.CBr_2.CH_3$. *Methyl bromacetol. Bromacetol. Acetone bromide.* (115°).

S.G. $\frac{15}{15}$ 1·8476; $\frac{25}{25}$ 1·8314. M. M. 10·137 at 20·7° (Perkin). Formed in small quantity from acetone and PBr_5 or PCl_3Br_2 (Linnemann, *A.* 138, 125; Friedel a. Ladenburg, *Z.* 1868, 48). Also from allylene and conc. HBr (Reboul, *C. R.* 74, 669); and from α-bromo-propylene and HBr.

Reactions.—1. *Water* at 160° gives acetone.—2. Zn and HCl give propane (Linnemann, *A.* 161, 67).—3. Alcoholic KOH gives α-bromo-propylene $CH_3.CBr{:}CH_2$.

ωω-Di-bromo-propane $CH_3.CH_2.CHBr_2$. (c. 130°). From ω-bromo-propylene $CH_3.CH{:}CHBr$ and conc. HBr (Reboul, *A. Ch.* [5] 14, 467).

$\omega_1\omega_2$-Di-bromo-propane $CH_2Br.CH_2.CH_2Br$. *Trimethylene bromide.* (165°). S.G. $\frac{0}{}$ 2·006 (Z.); $\frac{0}{}$ 2·018 (G.); $\frac{17.6}{4}$ 1·9228 (F.). S.V. 117·8 (Z.). Formed from $\omega_1\omega_1$-di-oxy-propane and HBr (Freund, *M.* 2, 639).

Preparation.—Allyl bromide is saturated with very nearly dry HBr at −16°, sealed up and left at 30° for 24 hours. The tube is opened and the operation repeated as long as any gas is absorbed (Geromont, *A.* 158, 370; Reboul, *A. Ch.* [5] 14, 472; Erlenmeyer, *B.* 12, 1354; *A.* 197, 184; Roth, *B.* 14, 1351; Bogomolitz, *Bl.* [2] 30, 23).

Reactions.—1. Alcoholic KOH forms allyl bromide or allyl ethyl oxide.—2. Alcoholic NH_3 forms some amorphous bases (Niederist, *M.* 3, 840).—3. Heated to 100° with Ag_2O and water it gives tri-methylene-glycol thus differing from the isomeric propylene bromide which gives propionic aldehyde (Beilstein a. Wiegand, *B.* 15, 1496).—4. Al_2Br_6 converts it into propylene bromide (Gustavson, *J. pr.* [2] 36, 303).

ωωα-Tri-bromo-propane $CH_3.CHBr.CHBr_2$. (201°). From ω-bromo-propylene and Br (Reboul, *A. Ch.* [5] 14, 481).

ωαα-Tri-bromo-propane $CH_3.CBr_2.CH_2Br$. (191°). S.G. $\frac{0}{}$ 2·35. Formed by the union of bromo-propylene with Br (Reboul, *A. Ch.* [5] 14, 481; C. Kolbe, *J. pr.* 133, 393).

s-Tri-bromo-propane $CH_2Br.CHBr.CH_2Br$. *Tri-bromhydrin.* [17°]. (220°). S.G. $\frac{23}{}$ 2·44.

Formation. — 1. From di-bromhydrin or epibromhydrin and PBr_5 (Berthelot a. de Luca, *A.* 101, 76; Henry, *A.* 154, 369).—2. From allyl bromide and Br (Tollens, *A.* 156, 168).—3. By bromination of isopropyl bromide (Linnemann, *A.* 136, 63).—4. From allyl iodide and Br (Wurtz, *A.* 104, 247).

Properties.—Prisms or liquid.

Reactions. — 1. Alcoholic KOH gives $CH{:}C.CH_2OEt$. — 2. Solid KOH gives two di-bromo-propylenes. — 3. AgOAc gives triacetin $C_3H_5(OAc)_3$.—4. KCy gives $C_3H_5(Cy)_3$.—5. Alcoholic NH_3 forms di-bromo-di-allyl-amine and then methyl-pyridine.

Tetra-bromo-propane $CH_3.CBr_2.CHBr_2$. *Allylene tetra-bromide.* (225°–230°); (110°–130°) at 10 mm. S.G. $\frac{0}{}$ 2·94. From allylene and Br (Oppenheim, *Bl.* [2] 2, 6; 4, 434; *A.* 132, 124). Liquid, decomposed by alcoholic KOH into HBr and tri-bromo-propylene (c. 193°) (Pinner, *A.* 179, 59).

Tetra-bromo-propane $CH_2Br.CBr_2.CH_2Br$. [195°]. From iso-allylene and Br (Hartenstein, *J. pr.* [2] 7, 317).

The following tetra-bromo-propanes have also been prepared:

(*a*): (251°); S.G. 2·64. From propylene bromide and Br (Reboul, *A. Suppl.* 1, 232).

(*b*): [69°]; (c. 235°). By brominating isopropyl bromide (Linnemann, *A.* 136, 64).

(*c*): (226°); S.G. 2·47. From propylene bromide and Br (Cahours, *A.* 76, 284).

Penta-bromo-propanes $C_3H_3Br_5$. The following have been described:

(*a*): (255°); S.G. 2·60. From propylene bromide and Br (Cahours, *C. R.* 31, 291).

(*b*): [173°]. From tri-bromo-propylene and Br (Pinner, *A.* 179, 60).

(*c*): $CHBr_2.CBr_2.CHBr_2$. S.G. $\frac{12}{}$ 3·01. From propargyl bromide and Br (Henry, *B.* 7, 761).

BROMO-PROPIOLIC ACID $CBr{:}C.CO_2H$. Formed by decomposing mucobromic acid with baryta (Jackson a. Hill, *B.* 11, 1675; *Am.* 3, 121). Prisms (from ether). V. e. sol. water (crystallising therefrom with *x*aq); may be partially sublimed at 100°. Boiling water liberates bromo-acetylene; boiling baryta forms bromo-acetylene and also malonic acid. The acid gives with di-bromo-acrylic acid a compound $C_3HBrO_2C_3Br_2H_2O_2$ [105°].

Salts.—BaA'_2xaq.—AgA'.

α-BROMO-PROPIONIC ACID $C_3H_5BrO_2$ *i.e.* $CH_3.CHBr.CO_2H$. [25°] (W.). (206° cor.). Formed by heating propionic acid (1 mol.) with Br (1 mol.) for several days at 150° (Friedel a. Machuca, *C. R.* 53, 408; *A.* 120, 286). Formed also from lactic acid and HBrAq at 100° (Kekulé, *A.* 130 16).

Reactions.—1. *Sodium-amalgam* forms propionic acid.—2. *Boiling water* and ZnO give lactic acid. The K salt changes slowly to lactate in cold aqueous solution.—3. Alcoholic NH_3 forms alanine.—4. Finely divided Ag at 150° gives s-di-methyl-succinic acid.

Ethyl ether EtA'. (162°); (130°) at 160 mm. S.G. $\frac{11}{}$ 1·40. From the acid (Bischoff, *A.* 206, 319). Also from lactic ether and PBr_5 (Henry, *A.* 156, 176). *Preparation.*—Propionic acid (300 g.) is converted into the bromide by adding amorphous phosphorus (31 g.) and slowly running in bromine (400 g.). After the evolution of HBr has ceased the mixture is brominated by heating to 40°–50° and slowly running in more bromine (640 g.). When the whole of the bromine has disappeared the bromo-propionyl bromide is converted into the ethyl ether by the addition of absolute alcohol. It is then treated with water, washed and fractionated. The yield from 300 g. of propionic acid amounts to 640 g. of boiling-point 150°–160° (Zelinsky, *B.* 20, 2026).

Bromide $CH_3.CHBr.CO.Br$. (155°). From propionyl bromide and Br; also from propionic acid, P, and Br (Weinig, *A.* 242, 163). $ZnMe_2$, followed by water, gives methyl isopropyl ketone and di-methyl-isopropyl-carbinol (Kashirski, *C. C.* 1881, 278).

Imide $(CH_3.CHBr.CO)_2NH$. [148°]. Formed by the action of water on the compound $(C_3H_5NBr_2)$ of propionitrile with Br (Engler, *A.* 142, 71). Needles, m. sol. hot water.

β-Bromo-propionic acid $CH_2Br.CH_2.CO_2H$. [62°]. Small glistening plates. Formed by heating hydracrylic acid with HBr at 120° (Beckurts a. Otto, *B.* 18, 227).

αβ-Di-bromo-propionic acid $CH_2Br.CHBr.CO_2H$. [64°]. (227°). S. 1945 (?19·45) at 11°; S. (ether) 304 (?3·04) at 10°.

Formation.—1. Got by oxidising di-bromo-propyl alcohol with HNO_3. The yield is bad (Münder a. Tollens, *B.* 5, 73; *A.* 167, 222).—2. Also by union of acrylic acid with Br (Caspary a. Tollens, *A.* 167, 256).—3. From acroleïn di-bromide and HNO_3 (Linnemann a. Penl, *B.* 8, 1097).—4. By the action of HBr upon α-bromo-acrylic and αα-di-bromo-propionic acids (Philippi a. Tollens, *A.* 171, 333).

Properties.—Monoclinic crystals (Haushofer, *J.* 1881, 687; Zepharovich, *J.* 1878, 693). It crystallises in two forms: tables [64°] and prisms [51°]; the latter slowly change into the former. The salts readily split off bromide, forming β-bromo-acrylic acid.

Reactions.—1. Converted into acrylic acid by KI and water, or by Zn and H_2SO_4 (*v.* Zotta, *A.* 192, 102; C. a. I.).—2. *Water* at 120° gives bromo-oxy-propionic acid (Melikoff, *J. R.* 13, 227).

Salts.—AgA'.—NH_4A'.—KA'.—CaA'_2 2aq.—SrA'_2 6aq.

Methyl ether MeA'. (205·8° cor.) (Weger, *A.* 221, 84).

Ethyl ether EtA'. (214·6° cor.).

Allyl ether C_3H_5A'. (215°–220°).

Propyl ether PrA'. (233° cor.).

αα-Di-bromo-propionic acid $CH_3.CBr_2.CO_2H$. [65°] (F. a. M.); [61°] (P. a. T.). (c. 224°). From α-bromo-propionic acid and Br (Friedel a. Machuca, *C. R.* 54, 220; Philippi a. Tollens, *B.* 6, 515). Trimetric tables.

Reactions.—1. Zn and H_2SO_4 reduce it to propionic acid.—2. Alcoholic KOH gives α-bromo-acrylic acid.—3. Ag_2O forms pyruvic acid.—4. Finely divided *silver* in benzene gives di-methyl-maleïc anhydride.—5. The salts are more stable than those of the preceding acid; but the silver salt warmed with water changes to pyruvic acid (Beckurts a. Otto, *B.* 18, 235).

Salts.—NH_4A' ½aq.—NaA'.—KA'aq.—BaA'_2 9aq.—CaA'_2 2aq.—SrA'_2 6aq.

Methyl ether MeA'. (c. 177°). S.G. $\frac{0}{}$ 1·904.

Ethyl ether EtA'. (191°). S.G. $\frac{0}{}$ 1·754.

Propyl ether PrA'. (c. 202°). S.G. $\frac{0}{}$ 1·684.

Isobutyl ether $PrCH_2A'$. (c. 216°). S.G. $\frac{0}{}$ 1·578.

ααβ-Tri-bromo-propionic acid $CH_2Br.CBr_2.CO_2H$. [95°].

Formation.—1. By oxidation of acroleïn bromide (Linnemann a. Penl, *B.* 8, 1097).—2. From α-bromo-acrylic acid and Br (Mauthner a. Suida, *M.* 2, 99; Michael a. Norton, *Am.* 2, 17).

Properties.—Monoclinic prisms: $a:b:c$ = 1·83:1:·315; β = 66°; m. sol. water, v. sol. alcohol and ether. On heating the Ba salt $CH_2:CBr_2$ is formed. Alcoholic KOH gives αβ-di-bromo-acrylic acid.

Salt.—BaA'_2 *x*aq: needles.

αββ-Tri-bromo-propionic acid $CHBr_2.CHBr.CO_2H$. [118°]. Prepared by heating αβ-di-bromo-acrylic acid for eight hours with conc. HBrAq (Hill a. Andrews, *Am.* 4, 180; *P. Am. A.* 17, 133). Rectangular plates, v. sol. hot water, ether, and alcohol.—AgA': small rhombic plates.—CaA'_2 2aq.

Tetra-bromo-propionic acid $C_2HBr_4.CO_2H$ *i.e.* $CHBr_2.CBr_2.CO_2H$. [120°]. Prepared by the combination of αβ-di-bromo-acrylic acid with Br. Triclinic prisms: v. e. sol. alcohol and ether. The Ba salt is decomposed by boiling water with formation of tri-bromo-ethylene. Alcoholic KOH gives tri-bromo-acrylic acid.

Salts.—AgA'.—KA' 2aq.—BaA'_2 ½aq.—CaA'_2 aq (Mauthner a. Suida, *M.* 2, 107; Hill a. Mabery, *P. Am. A.* 17, 140; *Am.* 4, 266; 5, 251).

αβ-DI-BROMO-PROPIONIC ALDEHYDE $CH_2Br.CHBr.CHO$. *Acroleïn dibromide.* (c. 82°) at 5 mm. (Grimaux a. Adam, *Bl.* [2] 36, 136). From acroleïn and Br (Aronstein, *A. Suppl.* 3, 185; Henry, *B.* 7, 1112; Linnemann a. Penl, *B.* 8, 1097). Pungent oil. Reduces Fehling's solution. Readily polymerises, becoming crystalline [84°] in presence of HCl. HNO_3 oxidises it to di- and tri-bromo-propionic acids.

Tri-bromo-propionic aldehyde. A liquid combination of this body with propyl alcohol $CBr_3.CH(OH)(OPr)$ appears to be formed on treating propyl alcohol with Br (Hardy, *C. R.* 79, 806).

γ-BROMO-*n*-PROPYL-ACETO-ACETIC ETHER $CH_2Br.CH_2.CH_2.CH(CO.CH_3).CO_2Et$. Liquid. Insol. water, sol. alcohol and ether. Heavier than water.

Preparation.—6 grms. of sodium are dissolved in 60 grms. of absolute alcohol and added to 32 grms. of aceto-acetic ether. The sodio-aceto-acetic ether is then added to 80 grms. of tri-methylene bromide and heated on the water-bath for half an hour; the yield is 75 p.c. of the theoretical.

Reactions.—By boiling with dilute acids it yields acetyl-butyl bromide and finally acetyl-butyl alcohol $CH_3.CO.CH_2.CH_2.CH_2.CH_2OH$. Alcoholic NH_3 eliminates HBr forming so-called 'tri-methylene-aceto-acetic ether' (Lipp, *B.* 18, 3277. *V.* also pp. 24 and 40 *supra*).

β-BROMO-PROPYL ALCOHOL C_3H_7BrO *i.e.* $CH_2Br.CH_2.CH_2OH$. *Bromhydrin of tri-methylene glycol.* (98°–112°) at 185 mm. S.G. $\frac{20}{}$ 1·537. S. 17 at 15°. From tri-methylene glycol (*s*-di-oxy-propane) and HBr (Frühling, *M.* 3, 697).

ω-Bromo-isopropyl alcohol $CH_3.CH(OH).CH_2Br$ (?). *Bromhydrin of Propylene glycol.* (145°–148°). From propylene oxide and HBr (Markownikoff, *Z.* 1870, 423).

αβ-Di-bromo-propyl-alcohol $CH_2Br.CHBr.CH_2OH$. *Dibromide of allyl alcohol.* (219°) (Weger, *A.* 221, 83). *V.* p. 134.

Methyl derivative $CH_2Br.CHBr.CH_2OMe$ (185°) (Henry, *B.* 5, 455).

Ethyl derivative $CH_2Br.CHBr.CH_2OEt$ (194°).

s-Di-bromo-isopropyl alcohol $CH_2Br.CH(OH).CH_2Br$. *Glycerin di-bromhydrin.* (219°). S.G. $\frac{18}{}$ 2·1. From glycerin and PBr_5 (Berthelot a. de Luca, *A. Ch.* [3] 48, 313; Reboul, *A. Ch.* [3] 60, 32). Also from glycerin and Br (Barth, *A.* 124, 349). *V.* also GLYCERIN.

DI-BROMO-PROPYL-AMINE $C_3H_7Br_2N$ *i.e.* $CH_2Br.CHBr.CH_2.NH_2$. From allylamine hydrochloride and Br. Oil. Salts.—B'HCl: needles.—$B'_2H_2PtCl_6$ (Henry, *B.* 8, 399).

BROMO-PROPYL-BENZENE *v.* BROMO-CUMENE.

Di-bromo-*p*-di-propyl-benzene $C_6H_2Br_2Pr_2$. [48°]. From di-propyl-benzene and Br (H. Körner, *A.* 216, 227). Needles or rectangular tables (from alcohol).

BROMO-PROPYL-BENZOIC ACID *v.* BROMO-CUMINIC ACID.

DI-BROMO-PROPYL BORATE

$B(O.CH_2.CHBr.CH_2Br)_3$. *Hexabromide of* ALLYL BORATE (*q.v.*). Oil.

BROMO-PROPYL BROMIDE *v.* DI-BROMO-PROPANE.

TETRA-BROMO-DI-PROPYL-CARBINOL *v.* *Tetra*-BROMO-HEPTYL-ALCOHOL.

BROMO-PROPYLENE C_3H_5Br *i.e.* $CH_3.CH:CHBr$. (60°). S.G. $\frac{20}{}$ 1·43. Formed, together with $CH_3.CBr:CH_2$, by heating propylene bromide with alcoholic KOH (Reboul, *A. Ch.* [5] 14, 479). One of the products obtained by boiling $\alpha\beta$-di-bromo-butyric acid with aqueous Na_2CO_3. HBr reunites with it forming chiefly propylene bromide, but the combination is very much slower than with its isomeride (48°). Alcoholic KOH gives allylene. Br forms $CH_3.CHBr.CHBr_2$ (201°).

a-**Bromo-propylene** $CH_3.CBr:CH_2$. (48°). S.G. $\frac{0}{}$ 1·39. Formed as above (Reynolds, *A.* 77, 122). Also by the action of alcoholic KOH on $CH_3.CBr_2.CH_3$ (Reboul); and by union of HBr with allylene (Reboul, *C. R.* 74, 669). Oil. Readily combines with HBr forming $CH_3.CBr_2.CH_3$. Br forms $CH_3.CBr_2.CH_2Br$ (191°). Mercuric acetate in HOAc at 100° forms acetone.

Bromo-propylene $CH_2Br.CH:CH_2$ *v.* ALLYL BROMIDE p. 135.

Di-bromo-propylene $C_3H_4Br_2$ *i.e.* $CH_2:CBr.CH_2Br$. (140°–143°). (*a*)-*Epi-dibromhydrin.* From $CH_2Br.CHBr.CH_2Br$ and solid KOH (Henry, *A.* 154, 371; *B.* 14, 401) or sodium in ether (Tollens, *A.* 156, 168). Converted by water at 130° into bromo-allyl alcohol.

Di-bromo-propylene $CHBr:CH.CH_2Br$. (152°). S.G. $\frac{11}{}$ 2·06. Formed, together with the preceding and propargyl bromide, from *s*-tri-bromo-propane and KOH (Reboul, *A. Suppl.* 1. 230; Henry, *B.* 5, 186, 452). Alcoholic $AgNO_3$ forms $CHBr:CH.CH_2NO_3$; AgOAc and potassium sulphocyanide also form β-bromo-allyl salts.

Di-bromo-propylene $CH_3.CBr:CHBr$. *Allylene di-bromide.* (132°). S.G. $\frac{0}{}$ 2·05. From allylene and Br (Oppenheim, *Bl.* [2] 2, 6; 4, 431; *A.* 132, 126). Also from $CH_3.CHBr.CHBr_2$ and AgOAc at 120° (Linnemann, *A.* 136, 56).

Tri-bromo-propylene $CH_3.CBr:CBr_2$ (?). (184°) (O.); (c. 193°) (P.). From allylene tetrabromide and alcoholic KOAc (O.) or aqueous NaOH (Pinner, *A.* 179, 59).

Tri-bromo-propylene $CH_2Br.CBr:CHBr$. S.G. $\frac{19}{}$ 2·53. *Propargyl tribromide.* From propargyl bromide and Br. Non-volatile oil (Henry, *B.* 7, 761).

Penta-bromo-propylene C_3HBr_5. From allyl bromide, Br, and I at 210°. Non-volatile oil (Merz a. Weith, *B.* 11, 2243).

BROMO-PROPYLENE-GLYCOL *v.* GLYCERIN.

BROMO-PROPYLENE-UREA $C_4H_7BrN_2O$ *i.e.* $CO{<}^{NH}_{NH}{>}C_3H_5Br$ (?). [120°]. Formed by warming an aqueous solution of di-bromo-propyl-urea (Andreasch, *M.* 5, 40). Silky needles; sl. sol. cold water.—B'HCl: [143°].—B'HBr: [158°].—$B'_2H_2PtCl_6$.

DI-BROMO-PROPYL-MALONIC ACID

$C_6H_8Br_2O_4$ *i.e.* $(CO_2H)_2.CH.CH_2.CHBr.CH_2Br$. [121°]. From allyl-malonic acid and Br in CS_2 (Hjelt, *A.* 216, 58; *B.* 15, 624). Needles in stars (from ether). V. e. sol. ether, m. sol. water. Boiled with baryta, it forms di-oxy-propyl-malonate of barium (*q. v.*).

BROMO-PROPYL-PHENOL *v.* BROMO-CUMENOL.

BROMO-PROPYL-THIOPHENE

$C_4SH_2(C_3H_7)Br$. (189°). Colourless oil. Formed by bromination of *n*-propyl-thiophene (Ruffi, *B.* 20, 1741).

Di-bromo-propyl-thiophene $C_4SH(C_3H_7)Br_2$. (248°). Oil. Formed by bromination of propyl-thiophene with 2 mols. of bromine. By further bromination it is converted into tetra-bromo-thiophene (Ruffi, *B.* 20, 1741).

DI-BROMO-PROPYL-UREA $C_4H_8Br_2N_2O$ *i.e.* $NH_2.CO.NH.CH_2.CHBr.CH_2Br$. [109°]. From allyl-urea and Br (Andreasch, *M.* 5, 38). Needles or leaflets, sl. sol. cold water. Decomposed by heating with water into the isomeric hydro-bromide of bromo-propylene-urea (*q. v.*).

BROMO-PYRIDINE C_5NH_4Br [3]. (174° i.V.). S.G. $\frac{0}{4}$ 1·645.

Formation. — 1. By brominating pyridine (Hofmann, *B.* 12, 990).—2. By the action of bromoform upon an alcoholic solution of pyrrol and NaOEt or upon potassium pyrrol in ether (Ciamician a. Silber, *B.* 18, 721; Ciamician a. Dennstedt, *G.* 12, 211; *B.* 15, 1173; Danesi, *G.* 12, 150).

Properties.—Alkaline liquid, sl. sol. water. Reduced to pyridine by zinc and HCl.

Salts. $B'_2H_2PtCl_6$ 2aq: yellow monoclinic crystals, $a:b:c = 1·207:1:1·188$. $\beta = 107° 7'$.—B'HCl.

Di-bromo-pyridine $C_5NH_3Br_2$ [2:6]. [111°]. (222°).

Formation.—1. From pyridine and Br (Hofmann, *B.* 12, 988).—2. Together with pyridine and mono-bromo-pyridine by the action of bromine on acetyl-piperidine (Hofmann, *B.* 16, 587; *cf.* Schotten, *B.* 15, 421).—3. From tropidine hydrobromide and bromine at 170° (Ladenburg, *A.* 217, 148), di-bromo-methyl-pyridine being first formed, and ethylene bromide being the other product.—4. Formed by heating the tri-carboxylic acid [206°].

Properties.—Long flat pearly needles, insol. cold water, sl. sol. cold alcohol. Very weak base (difference from bromo-pyridine).

Salt.—$B'_2H_2Cl_2PtCl_4$: golden yellow needles (Pfeiffer, *B.* 20, 1349).

Methylo chloride $C_5NH_3Br_2MeCl$. Formed by heating di-bromo-apophyllin (*q. v.*) with HCl (Anderson, *A.* 94, 358; Hofmann, *B.* 14, 1498; v. Gerichten, *A.* 210, 99). Moist Ag_2O liberates an alkaline hydroxide.—$B'_2Me_2PtCl_6$.

Di-bromo-pyridine $C_5NH_3Br_2$. [165°]. Formed by adding bromine to a boiling aqueous solution of pyridine-sulphonic acid. Long white needles. Begins to sublime at about 80°. Sol. water, alcohol, ether and benzene.—$B'_2H_2Cl_2PtCl_4$ 2aq: large orange needles, sl. sol. water (Fischer a. Reimerschmid, *B.* 16, 1184; *cf.* Königs, *B.* 17, 589).

DI-BROMO-PYRIDINE-BETAÏNE

$C_5NH_3Br_2{<}^{CH_2}_{O}{>}CO$. *Anhydride of di-bromo-oxy-pyridyl-acetic acid.* Formed by heating di-bromo-pyridine with chloro-acetic acid.—BHCl: colourless needles.—$B_2H_2Cl_2PtCl_4$: large soluble brown prisms (Gerichten, *B.* 15, 1253).

BROMO-PYRIDINE DI-CARBOXYLIC ACID v. BROMO-APOPHYLLENIC ACID.

Bromo-pyridine-di-carboxylic acid $C_5NH_2Br(CO_2H)_2$. [165°]. Formed, together with oxalyl-anthranilic acid, by oxidation of (*Py*)-bromo-quinoline with $KMnO_4$. Crystals. V. sol. water, alcohol, ether, &c. It evolves CO_2 at its melting-point, yielding bromo-pyridine-mono-carboxylic acid (bromo-nicotinic acid) [183°] (Claus a. Collischonn, *B.* 19, 2767).

Di-bromo-pyridine-tri-carboxylic acid $C_5NBr_2(CO_2H)_3$ [2:6:1:3:5]. [206° anhydrous]. Obtained by oxidation of di-bromo-*s*-tri-methyl-pyridine [81°] with $KMnO_4$. Flat plates (containing 4aq). V. sol. hot water, sl. sol. alcohol, nearly insol. ether. $FeSO_4$ gives a red colouration. Heated to 165° it gives a sublimate of di-bromo-pyridine [111°].

Salts.—AgA'''aq: crystalline powder.—$KH_3A'''_2$ 6aq: glistening colourless needles, sol. hot water.—$Cu_3A'''_2$ ½aq: microcrystalline blue powder (Pfeiffer, *B.* 20, 1347).

a-BROMO-a-PYRIDYL-(*Py.* 2)-PROPIONIC ACID $C_8H_8BrNO_2$ *i.e.* $C_5H_4N.CBrMe.CO_2H$. From the corresponding oxy- acid and PBr_5 in CS_2.

Salt.—$(C_8H_8BrNO_2)HAuBr_4$ (Hardy a. Calmels, *Bl.* [2] 48, 232).

DI-BROMO-PYROCATECHIN $C_6H_2Br_2(OH)_2$.

Di-methyl-ether $C_6H_2Br_2(OMe)_2$. [93°]. Prepared by bromination of the di-methyl-ether of pyrocatechin (Tiemann a. Koppe, *B.* 14, 2018). Formed also by the action of Br on veratric acid. Colourless prisms. Sol. alcohol, ether and benzene.

Tri-bromo-pyrocatechin $C_6HBr_3(OH)_2$.

Mono-methyl-ether $C_6HBr_3(OMe)(OH)$. *Tri-bromo-guaiacol* [102°]. White felted needles. Formed by bromination of guaiacol (Tiemann a. Koppe, *B.* 14, 2017).

Tetra-bromo-pyrocatechin $C_6H_2Br_4(OH)_2$ [1:2:3:4:5:6]. [193°]. Formed by bromination of pyrocatechin in chloroform solution. Colourless prisms (from acetic acid) or long fine needles (from alcohol). On oxidation it yields tetra-bromo-*o*-quinone $C_6Br_4O_2$. Bromine-water at 80° forms $C_{18}H_2Br_{10}O$ [139°] (Zincke, *B.* 20, 1777; *cf.* Stenhouse, *C. J.* 27, 586; 28, 6; Hlasiwetz, *A.* 142, 251).

TETRA-BROMO-PYROCOLL $C_{10}H_2Br_4O_2N_2$. Formed by heating pyrocoll with bromine at 100°. Small yellow needles. Insol. alcohol, ether, chloroform and toluene, almost insol. acetic acid. By boiling with KOH it yields di-bromo-pyrrol-carboxylic acid (Ciamician a. Silber, *B.* 16, 2388).

TRI-BROMO-PYROGALLOL $C_6H_3Br_3O_3$ *i.e.* $C_6Br_3(OH)_3$. *Tri-bromo-pyrogallic acid.* From tannin, glacial acetic acid and bromine at 100° (Stenhouse, *C. J.* 27, 586; 28, 7; Webster, *C. J.* 45, 207). From pyrogallol and Br (Hlasiwetz, *A.* 142, 250). Flat needles, sol. hot water. Bromine-water converts it into 'xanthogallol' $C_{18}H_4Br_{14}O_6$ [122°] whence alkalis form $C_{18}H_7Br_{11}O_9$ [130°] (S.).

β-BROMO-PYROMUCIC ACID $C_5H_3BrO_3$. *Bromo-furfurane carboxylic acid* [129°]. S. 1·26 at 20°. From either di-bromo-pyromucic acid [168°], or [192°] by reduction with zinc-dust and ammonia (Hill a. Sanger, *A.* 232, 58). On adding HCl the acid separates in matted needles. Silky needles (from water, separating at first as an oil). Sol. chloroform and benzene, sl. sol. light petroleum or CS_2. Dry Br forms di-bromo-pyromucic acid [166°]. Dilute H_2SO_4 gives bromo-fumaric acid [177°].

Salts.—BaA'_2 aq. S. 2·13 at 20°.—CaA'_2 3aq. S. 1·77 at 20°.—AgA'.—NaA'.—KA'.

Ethyl ether EtA' [29°] (235° i.V.).

Amide.—$C_5H_2BrO_2NH_2$. [156°]. Silky needles (from water).

(δ)-Bromo-pyromucic acid $C_5H_3BrO_3$. [184°]. S. ·22 at 16°.

Formation.—1. By the action of alcoholic KOH on the dibromide of pyromucic acid (Schiff a. Tassinari, *B.* 11, 842; *G.* 8, 297). An isomeride [155°] said to be formed at the same time has not been observed by others. The dibromide of pyromucic ether when saponified also produces di-bromo-pyromucic acid (Canzoneri a. Oliveri, *G.* 14, 172).—2. From pyromucic acid (20 g.) and Br (36 g.) at 100°, the yield being 50 p.c. of the theoretical (Hill a. Sanger, *A.* 232, 46; *B.* 16, 1130).

Properties.—Pearly leaflets (from water); sl. sol. cold water, cold benzene, and $CHCl_3$; m. sol. alcohol and ether. Aqueous bromine forms fumaric, and the two di-bromo-succinic acids, and di-bromo-furfurane tetrabromide $C_4H_2Br_6O$ [111°]. Dilute HNO_3 produces maleïc acid.

Salts.—KA'.—NaA'.—AgA'.—BaA'_2 4aq (H. a. S.): pearly plates. S. (of BaA'_2) 3·47 at 18°. —BaA'_2 2½aq (C. a. O.).—CaA'_2 3aq: clumps of prisms. S. (of CaA'_2) 1·07 at 20°.

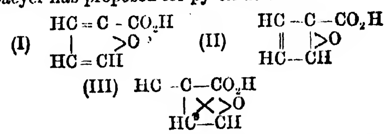
Ethyl ether EtA'. [17°]. (235° i. V.).

Amide $C_5H_2BrO_2(NH_2)$: [145°]; needles (from water).

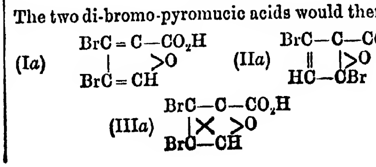
Tetrabromide $C_5H_3Br_5O_3$: [173°]; needles (from HOAc).

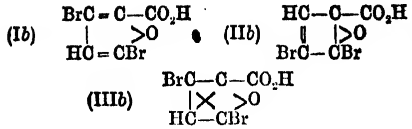
Di-bromo-pyromucic acids. Pyromucic acid combines with bromine forming a tetrabromide which when boiled with alcoholic NaOH forms a mixture of two di-bromo-pyromucic acids (βγ and βδ), (δ)-bromo-pyromucic acid and a tri-bromopyromucic acid (the latter from tetra-bromide of (δ)-bromopyromucic acid present in the crude bromide). The calcium salt of the (βδ) acid is ppd. from dilute (1 in 30) solutions of the mixed acids by NH_3 and $CaCl_2$. Of the remaining acids, the (δ) acid is present in very small quantity, while the tri-bromo- acid is very sparingly soluble in hot water (Hill a. Sanger, *A.* 232, 67; *B.* 17, 1759; *cf.* Tönnies, *B.* 11, 1085; 12, 1202; Canzoneri a. Oliveri, *G.* 14, 177).

Constitution.—(Hill a. Sanger, *A.* 232, 97). Baeyer has proposed for pyromucic acid

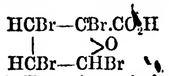


The two di-bromo-pyromucic acids would then be

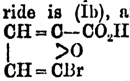
 and



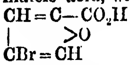
inasmuch as they are formed from the tetrabromide



by removing 2HBr. One of these acids produces, on oxidation with HNO_3, di-bromo-maleïc acid, the other gives mono-bromo-maleïc acid. Neither of the di-bromo-pyromucic acids derived from (II) could produce di-bromo-maleïc acid, hence that formula is disproved. Formula (III) is unusual in form. Assuming formula (I) ($\beta\gamma$)-di-bromo-pyromucic acid is represented by (Ia) while its ($\beta\delta$)-isomeride is (Ib), and (δ)-bromo-pyromucic acid is



, since on oxidation it gives maleïc acid, while (β)-bromo-pyromucic acid is



since it may be got by reducing either of the di-bromo-pyromucic acids. It will be noticed that in the preceding argument it has been assumed that the bromo-pyromucic acids are similar in constitution to pyromucic acid itself.

($\beta\gamma$)-di-bromo-pyromucic acid $C_5H_2Br_2O_3$ [192°]. S. ·21 at 20°. From the tetrabromide of pyromucic acid and alcoholic NaOH (see above). Short prisms grouped concentrically (from benzene) or bulky feathery crystals (from water). Sol. alcohol or ether, m. sol. chloroform, sl. sol. CS_2, boiling water or light petroleum (Hill a. Sanger, *A.* 232, 82).

Reactions.—1. Dry *bromine* forms tri-bromo-pyromucic acid.—2. *Bromine-vapour* passed into an aqueous solution of the acid forms tetra-bromo-furfurane, C_4Br_4O, [65°] and a little of a body $C_4H_2Br_2O_2$, [89°] (di-bromo-maleïc aldehyde). 3. Dilute HNO_3 on warming gives mucobromic and di-bromo-maleïc acids.—4. *Zinc-dust* and NH_3 from bromo-pyromucic acid [129°].

Salts.—AgA'.—NaA'2aq.—KA'.—$BaA'_2$3aq. S. ·35 at 20°.—$CaA'_2$5aq. S. 1·17 at 20°.

Ethyl ether.—EtA'. [68°]. M. sol. alcohol.

Amide $C_5HBr_2O_2NH_2$. [196°]. Slender needles (from dilute alcohol). Insol. CS_2 or light petroleum. Sl. sol. boiling water.

($\beta\delta$)-di-bromo-pyromucic acid $C_5H_2Br_2O_3$ [168°]. S. ·28 at 20°. From pyromucic acid and bromine at 100° (Hill a. Sanger, *A.* 232, 73). Also from the tetrabromide of pyromucic acid and alcoholic NaOH (see above). Small prisms, often in twins (from water). Very soluble in alcohol, ether, and boiling chloroform, less in benzene, sparingly in CS_2 or light petroleum.

Reactions.—1. Aqueous *bromine* in the cold forms bromo-maleyl bromide.—2. Dilute HNO_3 forms bromo-fumaric acid, bromo-maleïc acid probably being an intermediate product of the reaction.

Salts.—BaA'_2aq. S. ·10 at 16°.—$CaA'_2$3aq. S. ·30 at 17°.—AgA'.—NaA' 2aq.—KA'.

Ethyl ether EtA'. [58°]. (271° i.V. with decomposition). V. sol. ether, chloroform, benzene, and boiling alcohol, m. sol. cold alcohol or CS_2.

Bromide.—$C_5HBr_2O_2$.Br. [46°]. (c. 154°) at 24 mm. One of the products of the action of bromine upon pyromucic acid.

Amide $C_5HBr_2O_2NH_2$ [176°]. Silky needles.

Tri-bromo-pyromucic acid $C_5HBr_3O_3$. [219°]. S. ·072 at 19°. From the tetrabromide of (δ)-bromo-pyromucic acid and alcoholic NaOH (Hill a. Sanger, *A.* 232, 91). Some tri-bromo-furfurane is also formed. Small needles united in clumps. V. sol. alcohol and ether, sl. sol. chloroform or benzene, nearly insol. CS_2, light petroleum or cold water.

Reactions.—1. Water and *bromine* form tetra-bromo-furfurane [64°], thus: $C_5HBr_3O_3 + Br_2 = C_4Br_4O + CO_2 + HBr$.—2. Dilute HNO_3 forms di-bromo-maleïc acid.

Salts.—$BaA'_2$3aq. S. (of BaA'_2) ·20 at 20°.—$CaA'_2$4aq. S. (of CaA'_2) ·56 at 20°.—AgA'.—NaA'aq.—KA'aq.

Ethyl ether EtA'. [104°]. Rectangular prisms (from alcohol).

Amide $C_5Br_3O_2NH_2$. [223°]. Slender needles. Almost insol. CS_2, light petroleum or water, m. sol. ether, chloroform or benzene, v. sol. alcohol.

Ita-BROMO-PYROTARTARIC ACID $C_5H_7BrO_4$ *i.e.* $CH_2Br.CH(CO_2H).CH_2.CO_2H$. *Bromo-methyl-succinic acid.* [137°]. (c. 250°). From itaconic acid and conc. HBrAq at 0° (Beer, *A.* 216, 79; *cf.* Fittig, *A.* 188, 73; Swarts, *Z.* 1866, 722). Monoclinic crystals, v. sol. hot water. Boiling Na_2CO_3Aq gives itaconic and itamalic acids; boiling water produces paraconic acid.

Ethyl ether Et_2A''. (270°-275°).

***Citra*-bromo-pyrotartaric acid** $C_5H_7BrO_4$. [148°]. From citraconic anhydride and conc. HBrAq at 0°. Also from mesaconic acid and fuming HBrAq at 140° (F.). Monoclinic crystals. Decomposed by heating alone or with Na_2CO_3Aq into methacrylic acid, CO_2, and HBr. The silver salt on heating with water at 130° gives off allylene CH:C.CH_3 (Bourgoin, *Bl.* [2] 28, 459).

Bromo-pyrotartaric acid $C_5H_7BrO_4$ [204°]. White prisms. Formed together with bromo-crotonic acid by the action of Br on propane-tricarboxylic acid $CH_3.CH(CO_2H).CH(CO_2H)_2$ (*q. v.*) (Bischoff a. Guthzeit, *B.* 14, 616).

***Ita*-di-bromo-pyrotartaric acid** $C_5H_6Br_2O_4$. From itaconic acid, Br, and water (Kekulé, *A. Suppl.* 1, 339). Crystals, v. sol. water, alcohol, and ether.

Reactions.—1. *Sodium-amalgam* reduces it to pyrotartaric acid.—2. Moist Ag_2O forms di-oxy-pyrotartaric acid.—3. Boiling aqueous Na_2CO_3 forms aconic acid.

Anhydride $C_5H_4Br_2O_3$. [50°]. Formed by adding Br to a solution of itaconic acid in chloroform (Petri, *B.* 14, 1637).

***Citra*-di-bromo-pyrotartaric acid** $CO_2H.CBr_2.CHMe.CO_2H$. [150°]. S. 133 at 13°. From citraconic acid and Br (Kekulé, *A. Suppl.* 2, 86; Krusemark, *A.* 206, 1). Groups of needles; v. e. sol. water, alcohol, and ether. Heated with water or aqueous Na_2CO_3 it yields propionic aldehyde, bromo-propionic aldehyde, bromo-methacrylic acid, and HBr.—CaA''.

Anhydride $C_5H_4Br_2O_3$. From citraconic

anhydride and Br; formed also by heating the following acid with water.

Mesa-di-bromo-pyrotartaric acid $CO_2H.CHBr.CBrMe.CO_2H$. [194°] and [204°]. S. 31·5 at 13°. From mesaconic acid and Br on warming (Kekulé, *A. Suppl.* 2, 102; Fittig, *A.* 188, 86; 206, 1). Nodules. Heated with Na_2CO_3Aq it gives propionic aldehyde, two bromo-methacrylic acids, CO_2, and HBr. Heated with water it gives propionic aldehyde and bromo-citraconic anhydride.

Di-bromo-pyrotartaric acid [102°]. Formed by brominating pyrotartaric acid (Reboul a. Bourgoin, *Bl.* [2] 27, 348).

Di-bromo-pyrotartaric acid [128°]. From propane tri-carboxylic acid and Br (Bischoff a. Emmert, *B.* 15, 1107).

Tri-bromo-pyrotartaric acid $C_5H_5Br_3O_4$. From pyrotartaric acid, Br, and water at 120° (Lagermark, *Z.* 1870, 299). Hexagonal prisms; sublimes above 240°.—Ag_2A''.

TETRA-BROMO-PYROTRITARIC ACID $C_7H_4Br_4O_3$. *Tetra-bromo-uvic acid.* [162°]. Obtained by exposing powdered dry pyrotritaric acid to the vapour of dry bromine at the ordinary temperature. Large colourless crystals. V. sol. alcohol, ether, acetone, acetic acid, chloroform, benzene, and CS_2, insol. water and petroleum-ether. The bromine is removed by alkalis and by aniline. By sodium-amalgam in slightly acid solution it is reduced back to pyrotritaric acid. By the action of an excess of bromine at 100° it yields penta-bromo-pyrotritaric acid.

Tetra-bromide $C_7H_4Br_8O_3$: [180°]. Formed by dissolving tetra-bromo-pyrotritaric acid in an excess of dry bromine. Small prisms; v. sol. acetic acid, sl. sol. benzene, chloroform, and CS_2, insol. water and ligroïn. Decomposed by alkalis. Reduced to pyrotritaric acid by sodium amalgam (Dietrich a. Paal, *B.* 20, 1078).

Penta-bromo-pyrotritaric acid $C_6H_2Br_5O(CO_2H)$. [c. 197°]. Obtained by heating the tetra-bromo-derivative with excess of bromine at 100°. White glistening crystals. V. sol. ordinary solvents except water and ligroïn (Dietrich a. Paal, *B.* 20, 1082).

TRI-BROMO-PYRROL-(α)-CARBOXYLIC ACID $C_4NHBr_3(CO_2H)$. *Tri-bromo-(α)-carbopyrrolic acid.* Long colourless needles. V. sol. alcohol, ether, acetone, sl. sol. hot water, insol. petroleum-ether. The methyl ether is formed by bromination of the methyl ether of pyrrol-(α)-carboxylic acid.

Methyl ether A'Me: [210°]. Long slender needles, v. sol. ether and hot alcohol, sl. sol. benzene and petroleum-ether, insol. water (Ciamician a. Silber, *B.* 17, 1153).

Di-bromo-pyrrol di-carboxylic acid. *Methyl ether* $C_4NHBr_2(CO_2Me)_2$. [222°]. From dimethyl pyrrol di-carboxylate and Br (Ciamician a. Silber, *G.* 17, 249). Long white needles; insol. water, sol. ether and hot alcohol. Converted by cold fuming HNO_3 into $C_4H_1BrNO_4$ [c. 171°].

BROMO-PYRRYL METHYL KETONE $CH_3.CO.C_4H_2BrNH$. *Pseudo-acetyl-bromo-pyrrol.* [108°]. Long colourless needles; obtained by bromination of pyrryl methyl ketone (Ciamician a. Dennstedt, *B.* 16, 2354).

Di-bromo-pyrryl methyl ketone $CH_3.CO.C_4HBr_2NH$. [144°], white needles. Formed by bromination of pyrryl methyl ketone.

Tri-bromo-pyrryl methyl ketone $C_6H_4Br_3ON$. [179°]. White silky needles. Sol. hot alcohol, ether, and aqueous alkalis, insol. water. Formed by the action of bromine upon pyrryl methyl ketone in aqueous solution (Ciamician a. Silber, *B.* 18, 1765).

Penta-bromo-pyrryl methyl ketone $C_6H_2Br_5ON$. [200°]. Small white needles. Formed by bromination of the tri-bromo-derivative dissolved in acetic acid (C. a. S., *B.* 18, 1765) or of pyrryl methyl ketone (C. a. D.).

BROMO-PYRUVIC ACID $C_3H_3BrO_3$ *i.e.* $CH_2Br.CO.CO_2H$. From pyruvic acid, Br, and water at 100° (Wichelhaus, *B.* 1, 265). Syrup.

Di-bromo-pyruvic acid $CHBr_2.CO.CO_2H$. [91°] (W.); [93°] (C.). From pyruvic acid (15g.), water (10g.), and Br (45g.) at 100° (Böttinger, *B.* 14, 1236; *cf.* Grimaux, *Bl.* [2] 21, 391; Clermont, *Bl.* [2] 19, 103; Wislicenus, *A.* 148, 208). Monoclinic efflorescent tables (containing 2aq); sol. water and ether. Baryta converts it into tartronic acid. Benzene and conc. H_2SO_4 form $CHBr_2.C(OH)Ph.CO_2H$ (Böttinger, *B.* 14, 1235).—Di-bromo-pyruvic acid (1 mol.), urea (1 mol.) and conc. H_2SO_4 form di-bromo-pyruvureïde $C_4H_4Br_2N_2O_2$, whence bromine-water forms tri-bromo-pyruvurin $C_4Br_3N_2O_3H_3$, a body which is decomposed by cold ammonia into bromoform and ammonic oxalurate. Ammonia converts di-bromo-pyruvureïde into di-bromo-pyruvuramide $C_4H_5Br_2N_3O_2$ which is decomposed by boiling baryta-water into NH_3, urea, HBr, tartronic acid, and amido-uracil $C_4H_5N_3O_2$ (E. Fischer, *A.* 239, 185).

Tri-bromo-pyruvic acid $CBr_3.CO.CO_2H$. [90°], [101°, hydrated]. Formed, together with the preceding, by brominating pyruvic acid (Grimaux, *Bl.* [2] 21, 390). Also from lactic acid and Br. Laminæ resembling naphthalene (containing 2aq); sl. sol. cold water. Decomposed by boiling water into bromoform and oxalic acid.

Ethyl ether EtA'. [97°]. Formed by adding Br to a solution of lactic acid in ether (Klimenko, *J. R.* 8, 125; Wislicenus, *A.* 143, 10).

DI-BROMO-PYRUVURAMIDE $C_4H_5N_3Br_2O_2$. *Di-bromo-pyvuramide.* [170°-180°]. From di-bromo-pyruvureïde and conc. NH_3Aq in the cold (Fischer, *A.* 239, 191). Slender needles (from alcohol). V. sol. warm water, but slowly decomposed by boiling water. Decomposed by boiling baryta-water into NH_3, urea, HBr and tartronic acid, another portion forming amido-uracil.

DI-BROMO-PYRUVUREÏDE $C_4H_4Br_2N_2O_2$. *Di-bromo-pyvureïde.* From di-bromo-pyruvic acid (*q.v.*), urea, and conc. H_2SO_4 (Fischer, *A.* 239, 188). Granular crystals (from HOAc), v. sl. sol. alcohol, water, and acids; sol. dilute alkalis. Decomposed by boiling alkalis. Decomposed by heat above 280°. Its ammonium and guanidine salts are sl. sol. water.

TRI-BROMO-PYRUVURIL ANHYDRIDE $C_5H_3Br_3N_4O_2$. *Tri-bromo-anhydro-pyvuril.* [180°]. Formed by heating tri-bromo-pyruvic acid and urea at 100° (Grimaux, *A. Ch.* [5] 11, 373). Light needles (from water).

TRI-BROMO-PYRUVURINE $C_4H_3Br_3N_2O_3$ *i.e.* $CBr_3.CO.CO.NH.CO.NH_2$. *Ureïde of tri-bromo-pyruvic acid. Tri-bromo-pyvurine.* [247°]

From di-bromo-pyruvureïde and excess of bromine-water at 100° or HNO_3 (S.G. 1·4) (Fischer, *A.* 239, 189). Glittering plates, m. sol. boiling water and alcohol, v. sl. sol. ether. Decomposed even by cold alkalis into bromoform and ammonium oxalurate.

(*B.* 2)-**BROMO - QUINOLINE** C_9H_6BrN *i.e.* $C_6H_3Br(C_3H_3N)$. *Benz-bromo-quinoline.* (278°). Liquid. Volatile with steam. Prepared by heating *p*-bromo-aniline with glycerin, nitrobenzene and H_2SO_4; the yield is 80 p.c.

Salts.—B'HCl: small white needles.—$(B'HCl)_2PtCl_4$: microscopic needles (La Coste, *B.* 15, 558).

Bromo-quinoline C_9H_6BrN. (270°). Yellowish oil. Prepared by bromination of quinoline. Perhaps identical with the preceding.

Salts. — B'HCl: monoclinic prisms. $(B'HCl)_2PtCl_4$: fine orange-red needles.

Methylo-iodide $C_9H_6BrNMeI$. By the action of Ag_2O on an aqueous solution of the iodide, a strongly alkaline solution of the hydrate is produced ($C_9H_6BrNMeOH$); this is transformed on standing or warming, by splitting off H_2O, into the much more stable methylo-oxide.

Methylo-oxide $(C_9H_6BrNMe)_2O$. [147°]. This is also formed by the action of KOH on the iodide. Colourless needles. Soluble in hot alcohol, sparingly in cold, very slightly soluble in water and ether. Combines with acids very slowly (La Coste, *B.* 14, 915; 15, 188).

(*Py.* 1 or 2)-**Bromo-quinoline** $C_6H_4<\begin{matrix}CBr:CH \\ | \\ N : CH\end{matrix}$ or $C_6H_4<\begin{matrix}CH:CBr \\ | \\ N : CH\end{matrix}$. (274° uncor.). Formed, together with propyl bromide, propylene bromide, quinoline hydrobromide, &c., by heating the propylo-bromide of quinoline di-bromide to 170°-190°. Prepared by heating to 180° the hydrobromide of quinoline di-bromide: $C_9H_7Br_2N,HBr = C_9H_6BrN,HBr + HBr$; the quinoline-di-bromide is formed by the action of bromine on an ethereal solution of quinoline. Oil of aromatic smell resembling quinoline. On oxidation with $KMnO_4$ it yields oxaloxyl-anthranilic acid $C_6H_4(CO_2H).NH.CO.CO_2H$ and bromo-pyridine-di-carboxylic acid $C_5H_2BrN(CO_2H)_2$.

Salts.—B'HCl: needles or tables; sublimes without melting.—B'HBr: foursided tables or prisms; sublimes at c. 190° without melting; sol. alcohol, sl. sol. cold water.—$B'HNO_3$×: [180° uncor.]; small concentric prisms.—$B'_2H_2SO_4$×: [183° uncor.]; small needles; dissociated by water.—$B'_2H_2Cr_2O_7$: [145°]; sparingly soluble flat yellow prisms (from hot water).—$B'_2H_2Cl_2PtCl_4$: small orange-yellow needles.—B'_2AgNO_3: [173°]; needles (Claus a. Collischonn, *B.* 19, 2763).

(*B.*1:4)-**Di-bromo-quinoline** $\begin{matrix}CH:CBr \\ CH:CBr\end{matrix}>C_5H_3N$. [128°]. (α)-*Di-bromo-quinoline.*

Formation.—1. By bromination of quinoline by heating the hydrochloride with bromine at 180° (La Coste, *B.* 14, 917; 15, 191).—2. By heating di-bromo-aniline [1:4:5] with a mixture of glycerine, nitrobenzene and H_2SO_4 (Metzger, *B.* 17, 186).

Properties.—Distils without decomposition. Volatile with steam. Long white needles. Almost insol. water, v. sol. alcohol, ether, benzene and aqueous acids.

Salts. — B'HCl: small needles. — $B'_2H_2Cl_2PtCl_4$: fine yellow needles.—$B'_2H_2Cr_2O_7$: orange-red microcrystalline powder, decomposed by water into the base and CrO_3. The picrate forms long yellow needles, decomposed by water.

Methylo-iodide B'MeI: Slender red needles. Sol. hot water, insol. ether and cold alcohol.

Methylo-oxide B'_2Me_2O. Formed by the action of NaOH on the iodide. Microscopic needles.

(*B.* 2, 4)-**Di-bromo-quinoline** $C_6H_2Br_2(C_3H_3N)$. [101°]. Slender colourless needles. Volatilises undecomposed. Formed by heating di-bromo-aniline with glycerin, nitrobenzene and H_2SO_4. $(B'HCl)_2PtCl_4$ (La Coste, *B.* 15, 559).

Di-bromo-quinoline (probably *B.* 2 : *Py.* 1) $C_9H_5Br_2N$. [124° uncor.] Formed by the action of bromine (2 mols.) upon quinoline-(*B.* 2)-sulphonic acid (1 mol.) in cold aqueous solution. Long colourless needles (from ether). Sublimable. It is oxidised by $KMnO_4$ to bromo-pyridine-di-carboxylic acid [165°] (Claus a. Küttner, *B.* 19, 2884).

Di-bromo-quinoline tetrahydride $C_9H_9Br_2N$. [66° uncor.]. Formed by reduction of tetra-bromo-quinoline with sodium amalgam. Colourless tables. Volatile with steam. Sol. alcohol and ether, insol. water.

Salts.—B'HCl: [75°], acicular crystals.—$(B'HCl)_2PtCl_4$ 2aq: yellow crystalline powder.—$B'HNO_3$: [189°]: prisms.—$B'H_2SO_4$: white plates, decomposes at 246° uncor.—$B'H_2C_2O_4$: colourless tables, decomposes at 171° uncor. (Claus a. Istel, *B.* 15, 822).

Tri-bromo-quinoline $C_9H_4Br_3N$. [170° uncor.]. Formed by the action of bromine (3 mols.) upon an aqueous solution of quinoline-(*B.* 2)-sulphonic acid (1 mol.) at 100°. Long silky needles. Sl. sol. cold ether (Claus a. Küttner, *B.* 19, 2885).

Tri-bromo-quinoline $C_9H_4Br_3N$. [175°]. From quinoline and Br (Lubavin, *A.* 155, 318). Silky needles; v. sol. hot alcohol. Possibly identical with the preceding.

Tri-bromo-quinoline $C_9H_4Br_3N$. [198° uncor.]. Formed by the action of bromine upon an aqueous solution of quinoline-(*B.* 4)-sulphonic acid at 100°. White felted silky needles. V. sol. ether and hot alcohol. Sublimable (Claus a. Küttner, *B.* 19, 2882).

Tetra-bromo-quinoline $C_9H_3Br_4N$ [119° uncor.]. Long colourless needles or thick prisms. Insoluble in water. Formed by bromination of quinoline in CS_2 (Claus a. Istel, *B.* 15, 820).

Hexa-bromo-quinoline C_9HBr_6N. [90°]. From pyridine (2, 3)-di-carboxylic acid, Br, and water (Weidel, *A.* 173, 95). Needles (from alcohol). Reduced to quinoline by sodium amalgam.

(*B.* 4)-**BROMO-QUINOLINE** (*B.* 1)-**CARBOXYLIC ACID** $C_9H_5BrN(CO_2H)$. [275°]. From bromo-amido-benzoic acid $C_6H_3Br(NH_2).CO_2H$ [1:2:4] (10g.), glycerin (22·5g.), *o*-nitro-phenol (6g.), and H_2SO_4 (20g.) by heating for 5 hours at 160° (Lellmann a. Alt, *A.* 237, 313). White powder, v. sl. sol. water and ether, sl. sol. hot alcohol. Salt.—$(HA')_2H_2PtCl_6$4aq.

(α)-**BROMO-QUINOLINE-SULPHONIC ACID** $C_9H_5(Br)N(SO_3H)$. S. ·08 at 22°; ·9 at 100°. Short thin needles. Sl. sol. alcohol. Formed together with the β-acid by sulphonating bromo-quinoline.

Salts.—$A'_2Mn\,4aq$: small yellow needles.—$A'Ag$: spangles or needles.—$A'K$: short prisms, S. 1·37 at 17°.—$A'NH_4$*: felted needles.—A'_2Ba: nearly insoluble crystalline pp.—$A'_2Mg\,10aq$: colourless plates.—$A'_2Zn\,4aq$: thin colourless needles (La Coste, *B.* 15, 1910).

(β)-**Bromo-quinoline-sulphonic acid** $C_9H_5N(Br)(SO_3H)$. S. ·15 at 22°; 2·75 at 100°. Short thick needles (containing aq). Formed together with the (α)-acid by sulphonation of bromo-quinoline.

Salts.—$A'K\,1\frac{1}{2}aq$: large tables, S. 17·25 at 22°.—$A'Ag$: colourless needles.—$A'_2Ba\,2aq$: sparingly soluble needles.—$A'_2Mg\,9aq$: small needles.—$A'_2Zn\,9aq$: six-sided tables.—$A'_2Mn\,6aq$: colourless tables (La Coste, *B.* 15, 1915).

BROMO-QUINONE $C_6H_3BrO_2$. [56°]. Formed by oxidising bromo-hydroquinone with Fe_2Cl_6 (Sarauw, *A.* 209, 106). Groups of needles, v. sol. alcohol, ether, and benzene, sl. sol. hot water. Ammonia gives a green colouration, turning black on warming.

Di-bromo-quinone $C_6H_2Br_2O_2$. [188°]. Formed by oxidation of di-bromo-hydroquinone (S.; Benedikt, *M.* 1, 346). Small golden crystals, insol. water, sol. alcohol, ether, and benzene. Boiling KOHAq gives di-bromo-di-oxy-quinone (dibromanilic acid).

Di-bromo-quinone $C_6H_2Br_2O_2$. [76°].

Formation.—Di-bromo-*p*-diazo-phenol, $C_6H_2Br_2{<}^{O}_{N_2}$, is converted by a boiling solution of calcium chloride into di-bromo-hydroquinone, $C_6H_2Br_2(OH)_2$. This solution is mixed with Fe_2Cl_6 and distilled, when the quinone passes over. The yield is small.

Properties.—Long, extremely slender needles, sol. in alcohol, ether, $CHCl_3$, CS_2, benzene, and alkalis. Pungent. May be sublimed (Böhmer, *J. pr.* 132, 465).

Di-bromo-quinone $C_6H_2Br_2O_2$. [122°]. From tri-bromo-phenol and fuming HNO_3 at 0° (Levy a. Schultz, *A.* 210, 158). Yellow laminæ (from dilute alcohol).

Di-bromo-quinone ? [88°]. From quercite and HBrAq at 160° (Prunier, *A. Ch.* [5] 15, 67). Three di-bromo-quinones are indicated by theory.

Tri-bromo-quinone $C_6HBr_3O_2$. [147°]. Formed by oxidising tri-bromo-hydroquinone in dilute alcoholic solution (Sarauw, *A.* 209, 120). Golden leaflets (from alcohol); sol. alcohol, ether, and benzene. Alkalis give a green colouration, followed by separation of red prisms. Boiling conc. NaOH gives di-bromo-di-oxy-quinone and tri-bromo-hydroquinone. A tri-bromo-quinone [108°] is got by heating quercite with HBr (P.). A tri-bromo-quinone is also formed by reduction of tetra-bromo-quinone (Stenhouse, *A. Suppl.* 8, 20; *cf.* Herrmann, *B.* 10, 110).

Tetra-bromo-quinone $C_6Br_4O_2$. *Bromanil.*

Formation.—1. By treating phenol with Br and I (Stenhouse, *C. J.* 23, 10).—2. By boiling picric acid with Br and water (Stenhouse, *A.* 91, 307).—3. From quinone and Br (Sarauw, *B.* 12, 680, *A.* 209, 126).—4. A product of the action of Br and water on benzoic acid (Hübner, *A.* 143, 255), and on proteïds (Hlasiwetz a. Habermann, *A.* 159, 320).—5. From tri-bromo-phenol and HNO_3 (Losanitsch, *B.* 15, 474).—6. From di-oxy-di-hydro-terephthalic (succinylo-succinic) acid and Br (Herrmann, *A.* 211, 341).—7. From (1,3,5,4)-bromo-di-nitro-phenol by heating with Br (Ling, *C. J.* 51, 147).

Properties.—Golden laminæ (from HOAc); sublimes as sulphur-yellow crystals. Insol. water, m. sol. boiling alcohol, sl. sol. ether. HIAq reduces it to tetra-bromo-hydroquinone. Potash forms a greenish-black solution turning purple.

Tetra-bromo-*ortho*-quinone $C_6Br_4O_2$ [1:2:3:4:5:6]. [151°]. Obtained by oxidation of tetra-bromo-pyrocatechin in acetic acid solution with HNO_3. It can also be prepared directly from pyrocatechin by adding bromine (10 to 12 pts.) to a boiling solution of the latter (1 pt.) in acetic acid (20 pts.). Dark-red thick prisms, tables, or transparent plates. V. sol. alcohol, ether, acetic acid, and benzene, sl. sol. petroleum spirit. It is a powerful oxidising agent, being readily reduced to tetra-bromo-pyrocatechin. With aniline it gives a compound which crystallises in bluish-black glistening plates or thick needles [173°] (Zincke, *B.* 20, 1776).

DI-BROMO-QUINONE-CHLORIMIDE

$C_6H_2Br_2{<}^{NCl}_{O}$ $\left[2{:}6{:}^{4}_{1}\right]$. [80°] Long yellow prisms. Prepared by adding a solution of chloride of lime to an acidified solution of di-bromo-amido-phenol [2:6:4:1] (Möhlau, *B.* 16, 2845).

DI-BROMO-QUINONE-PHENOL-IMIDE

$N{<}^{C_6H_4.OH}_{C_6H_2Br_2.O}$ [4:2:6:1].

Formation.—1. By adding di-bromo-quinone chlorimide to an alkaline solution of phenol.—2. By oxidising an alkaline solution of di-bromo-amido-phenol [2:6:4:1] and phenol with $K_2Cr_2O_7$.

Properties.—Dark red prisms with metallic reflection. Sol. alcohol, ether and acetic acid with a magenta-red colour; insol. water.

Reactions.—On heating with HCl it is split up into quinone and di-bromo-amido-phenol. On reduction it yields di-bromo-di-oxy-di-phenyl-amine $HN{<}^{C_6H_4.OH}_{C_6H_2Br_2.OH}$.

Sodium salt $C_{12}H_6Br_2ON(ONa)$: long blue prisms with golden-green reflection. Soluble in water and alcohol with a blue colour. Heated with an excess of aqueous NaOH the blue colour changes to red, but reappears on cooling (Möhlau, *B.* 16, 2845).

BROMO-RESORCIN $C_6H_3Br(OH)_2$. [91°]. Formed by boiling bromo-di-oxy-benzoic acid with water for some hours (Zehenter, *M.* 8, 293). Groups of needles; v. sol. water and ether, m. sol. alcohol. Fe_2Cl_6 colours the aqueous solution bluish-violet, a red pp. being subsequently formed. Heated with water, K_2CO_3, and $SnCl_2$ it gives resorcin and di-oxy-benzoic acid.

Bromo-resorcin. *Di-propyl derivative* $C_6H_3Br(OPr)_2$. [71°]. Formed by brominating di-propyl-resorcin (Kariof, *B.* 13, 1679). Colourless silky needles; may be sublimed. V. sol. alcohol and HOAc; sl. sol. water.

Di-bromo-resorcin $C_6H_2Br_2(OH)_2$. [93°]. Formed, together with 'di-bromo-mono-resorcin phthaleïn,' by heating tetra-bromo-fluoresceïn (eosin) with dilute NaOHAq at 140° (Baeyer, *A.* 183, 57; Hofmann, *B.* 8, 64). Formed also by boiling di-bromo-(1,3,2)-di-oxy-benzoic acid with water (Zehenter, *M.* 2, 478; 8, 293). Needles (from water); m. sol. hot water, v. e. sol. alcohol and ether. Fe_2Cl_6 gives a transient violet colour.

Di-methyl ether $C_6H_2Br_2(OMe)_2$. [141°]. Slender needles. Insol. water, sol. alcohol and ether. Prepared by bromination of the dimethyl-ether of resorcin (Tiemann a. Parrisius, *B.* 13, 2365; *cf.* Honig, *B.* 11, 1041).

Di-bromo-resorcin $C_6H_2Br_2(OH)_2$. [112°]. From Br and resorcin in CS_2 (Zehenter, *M.* 8, 293). Colourless needles (containing aq) (from water); m. sol. hot water. Fe_2Cl_6 gives a blue colour followed by a dark pp.

Tri-bromo-resorcin $C_6HBr_3(OH)_2$. [104°] (Typke, *B.* 10, 1578). From resorcin, Br, and water (Hlasiwetz a. Barth, *A.* 130, 357), or Br, and HOAc (Benedikt, *M.* 4, 227). Formed also by heating penta-bromo-resorcin with aldehyde or formic acid (Claassen, *B.* 11, 1439). Small needles; sl. sol. water, v. sol. alcohol.

Mono-acetyl derivative $C_6HBr_3(OH)(OAc)$. [114°]. From mono-acetyl-resorcin and Br (C.); sol. hot water.

Di-acetyl derivative $C_6HBr_3(OAc)_2$. [108°]. From penta-bromo-resorcin and Ac_2O. Sol. hot water.

Mono-methyl ether $C_6HBr_3(OH)(OMe)$. [104°]. From mono-methyl-resorcin and Br. Slender white needles, sol. alcohol and ether, insol. water (Tiemann a. Parrisius, *B.* 13, 2364).

Tetra-bromo-resorcin $C_6Br_4(OH)_2$. [163°]. (C.); [167°] (B.). Formed by treating penta-bromo-resorcin with H_2SO_4 (Claassen, *B.* 11, 1440; Benedikt, *M.* 1, 366). Small needles (from alcohol).

Di-acetyl derivative $C_6Br_4(OAc)_2$. [169°]; v. sol. hot water.

Penta-bromo-resorcin $C_6Br_4(OH)(OBr)$? [114°]. Formed by adding an aqueous solution of resorcin to a cooled mixture of Br and water (Stenhouse, *A.* 163, 184). Dimetric crystals, $a:c = \cdot 6076:1$. V. sl. sol. water. Alcoholic $AgNO_3$ pps. more than two-thirds of its Br. At 160° it splits up into bromine and tri-bromo-resoquinone $C_6HBr_3O_2$ (Liebermann a. Dittler, *B.* 5, 1090; *A.* 169, 256). Converted into tri-bromo-resorcin by conc. HI, H_2S, $SnCl_2$, warm alcohol, aldehyde, or formic acid (Benedikt, *M.* 1, 351; Claassen, *B.* 11, 1433). Boiling Ac_2O gives di-acetyl-tri-bromo-resorcin. Aniline forms tri-bromo-aniline and tri-bromo-resorcin; phenol acts similarly (Benedikt, *B.* 11, 2168). Boiling dilute KOH produces bromoform.

Hexa-bromo-resorcin $C_6Br_4(OBr)_2$? [136°]. S.G. $\frac{16}{}$ 3·188. Prepared by heating tetra-bromo-resorcinol with excess of bromine. Monoclinic crystals: $a:b:c = \cdot 983:1:1\cdot 687$; $\beta = 85°36'$. Decomposed by alcohol forming tetra-bromo-resorcin (Benedikt, *M.* 1, 365).

TRI-BROMO-RESOQUINONE $C_6HBr_3O_2$ or $C_{12}H_2Br_6O_4$. Formed by heating penta-bromo-resorcin at 160° (Liebermann a. Dittler, *B.* 5, 1090). Orange needles; insol. water, v. sol. alcohol and ether. At 230° it gives off Br leaving amorphous $C_{12}H_2Br_4O_4$. Reduced by Sn and HCl to tetra-bromo-tetra-oxy-diphenyl (Benedikt, *M.* 1, 350; *B.* 11, 2170).

DI-BROMO-RESORCIN-PHTHALEÏN so-called $C_{14}H_8Br_2O_5$ *i.e.* $CO_2H.C_6H_4.CO.C_6HBr_2(OH)_2$ *Di-bromo-di-oxy-benzoyl-benzoic acid.* [220°]. Formed, together with di-bromo-resorcin, by heating tetra-bromo-fluoresceïn with dilute NaOHAq (Baeyer, *A.* 183, 56). Plates, v. sl. sol. water.

BROMO RETENE *v.* RETENE.

BROMO RICINELAIDIC ACID $C_{18}H_{33}BrO_3$. From the dibromide of ricinelaidic acid and alcoholic KOH. Oil. Alcoholic KOH forms an acid [71°] (Ulrich, *Z.* 1867, 549).

BROMO-RICINOLEIC ACID $C_{18}H_{33}BrO_3$. From ricinoleic acid by successive treatment with Br and alcoholic KOH (Ulrich, *Z.* 1867, 546). Oil; converted by alcoholic KOH into ricinstearolic acid $C_{18}H_{32}O_3$.

Di-bromo-ricinoleic acid $C_{18}H_{32}Br_2O_3$. From ricinstearolic acid and Br. Oil.

BROMO-ROSANILINE *v.* ROSANILINE.

TETRA-BROMO-ROSOLIC ACID $C_{20}H_{12}Br_4O_3$. From Br and rosolic acid in HOAc (Graebe a. Caro, *A.* 179, 201). Lustrous green plates, insol. water. Its alkaline solutions are violet.—$A''Ag_2$: dark violet pp.

Ethyl ether $A''Et_2$: [110°-115°], soluble in alcohol, ether, and benzene, insoluble in water (Ackermann, *B.* 17, 1627).

BROMO-ROSOQUINONE $C_{12}H_4Br_4O_2$ *i.e.*

$C_6H_2Br_2—O$
| | (?). Red and steel-blue crystals.
$C_6H_2Br_2—O$

Prepared by the oxidation of tetra-bromo-phenol-phthaleïn (5 pts.) dissolved in H_2SO_4 (250 pts.) with a mixture of HNO_3 (5 pts.) and H_2SO_4 (50 pts.).

Bromo-rosohydroquinone $C_{12}H_6Br_4O_2$ *i.e.*

$C_6H_2Br_2.OH$
| (?). *Tetra-bromo-di-oxy-diphenyl.*
$C_6H_2Br_2.OH$

[264°]. Sublimable. Prepared by the reduction of the corresponding quinone (Baeyer a. Schraube, *B.* 11, 1301).

BROMO-SALICYLIC ACID *v.* BROMO-*o*-OXY-BENZOIC ACID.

BROMO-SALICYLIC ALDEHYDE *v.* BROMO-*o*-OXY-BENZOIC ALDEHYDE.

BROMO-STEARIC ACID $C_{18}H_{35}BrO_2$. [41°]. S.G. $\frac{22}{}$ 1·0653. From stearic acid (7 pts.), bromine (4 pts.), and water at 135° (Oudemans, *J. pr.* 89, 195). Crystalline mass, insol. water, v. sol. alcohol and ether. The silver salt heated with water forms stearidic acid $C_{18}H_{34}O_2$.

Di-bromo-stearic acid $C_{18}H_{34}Br_2O_2$. From oleïc acid and Br (Overbeck, *A.* 140, 42). Oil. Alcoholic KOH forms bromo-oleïc and stearolic acids. Moist Ag_2O gives oxy-oleïc acid $C_{18}H_{34}O_3$ and di-oxy-stearic acid $C_{18}H_{36}O_4$.

Di-bromo-stearic acid $C_{18}H_{34}Br_2O_2$. [27°]. From elaidic acid and Br. Reduced to elaidic acid by sodium amalgam.

Tri-bromo-stearic acid $C_{18}H_{33}Br_3O_2$. From bromo-oleïc acid and Br. Oil.

Tetra-bromo-stearic acid $C_{18}H_{32}Br_4O_2$. [70°] From stearolic acid and Br. Laminæ (from alcohol).

BROMO-STILBENE *v.* BROMO-DI-PHENYL-ETHYLENE.

BROMO-STRYCHNINE v. STRYCHNINE.

ω-BROMO-STYRENE C_8H_7Br *i.e.* $C_6H_5.CH:CHBr$. *Bromo-phenyl-ethylene.* Formed by boiling styrene dibromide with alcoholic KOH or by heating it with water at 190° (Glaser, *A.* 154, 168; Radziszewski, *B.* 6, 493). Heavy pungent oil; decomposed by distillation. Converted by heating with water into phenyl-acetic aldehyde (Erlenmeyer, *B.* 14, 323).

α-Bromo-styrene $C_6H_5.CBr:CH_2$. [7°]. (220° i.V.).

Formation.—1. From styrene dibromide and alcoholic KOAc at 160° (Zincke, *A.* 216, 290).—2. By boiling αβ-di-bromo-phenyl-propionic acid with water (Barisch, *J. pr.* [2] 20, 179; Fittig a. Binder, *A.* 195, 141).—3. From bromo-oxy-phenyl-propionic acid and water at 200° (G.).

Properties. — Oil, with pleasant odour of hyacinths. May be distilled. Does not readily give up its Br. Converted into acetophenone by heating with water at 180° (Friedel a. Balsohn, *Bl.* [2] 32, 614).

Di-bromo-styrene $C_8H_6Br_2$. (254°). From tri-*exo*-bromo-β-phenyl-propionic acid and water at 100° (Kinnicutt a. Palmer, *Am.* 5, 381). Oil.

Tri-bromo-styrene $C_8H_5Br_3$. From the preceding and Br. Oil (K. a. P.).

BROMO-STYRENE DIBROMIDE v. DI-BROMO-ETHYL-BENZENE.

BROMO-SUBERIC ACID $C_6H_{11}Br(CO_2H)_2$. [103°]. Prepared, together with di-bromo-suberic acid, by the action of bromine and phosphorus on suberic acid. Crystalline powder. Sol. alcohol and ether. By alcoholic KOH it gives suberconic acid (Ganttner a. Hell, *B.* 15, 142).

Di-bromo-suberic acid $C_6H_{10}Br_2(CO_2H)_2$ [173°]. Formed by bromination of *n*-suberic acid. Glistening needles. V. sol. alcohol, ether, and hot water, v. sl. sol. benzene, chloroform, ligroïn, and cold water. By heating with alcoholic KOH it gives di-ethoxy-suberic acid together with a small quantity of subercolic acid $C_6H_8(CO_2H)_2$ (Hell a. Rempel, *B.* 18, 813).

BROMO-SUCCINIC ACID $C_4H_5BrO_4$ *i.e.* $CO_2H.CH_2.CHBr.CO_2H$. [160°]. S. 19·2 at 15·5°.

Formation.—1. By heating succinic acid (5g.) with Br (2½ c.c.) and water (40 c.c.) at 120° (Kekulé, *A.* 117, 125; Carius, *A.* 129, 6; Hell, *B.* 14, 892).—2. From succinic acid (5 g.), Br (2½ c.c.) and chloroform (5 c.c.) at 160° (Orlowsky, *J. R.* 9, 277).—3. From succinic ether and Br (Schacherl, *B.* 14, 637).—4. By the action of HBr on fumaric, tartaric, malic, and racemic acids (Kekulé, *A.* 130, 21; Fittig, *A.* 188, 88; Anschütz a. Bennert, *B.* 15, 643). 5. By decomposing its bromide with water (Volhard, *A.* 242, 153).

Properties.—Small prisms, v. sol. water. Its silver salt rapidly decomposes. Moist Ag_2O gives malic acid. Sodium-amalgam produces succinic acid. Boiling water slowly forms fumaric acid.

Anhydride $C_4H_3BrO_3$. [31°]. (137°) at 11 mm. From the acid and AcCl at 100° (A. a. B.). Decomposed by heat into HBr and maleïc anhydride.

Methyl ether Me_2A''. (c. 134°) at 30 mm.

Ethyl ether Et_2A''. (226°). Inflames the skin. Cold aqueous or alcoholic NH_3 convert it into fumaramide. Aqueous NH_3 at 110° gives asparagine (Körner a. Menozzi, *G.* 17, 171).

Bromide $C_2H_3Br(COBr)_2$. Formed by adding Br (1100 g.) gradually to a mixture of succinic anhydride (300 g.) and amorphous P (36 g.) (Volhard, *A.* 242, 151).

s-Di-bromo-succinic acid $CO_2H.CHBr.CHBr.CO_2H$. S. 2·04 at 100°.

Formation.—1. By heating succinic acid (12 g.) with Br (11 c.c.) and water (12 c.c.) at 180° (Kekulé, *A.* 117, 123; *Suppl.* 1, 131; Bourgoin, *Bl.* [2] 19, 148).—2. From fumaric acid and Br (K.; Baeyer, *B.* 18, 676).

Properties. — Opaque prisms, sl. sol. cold water, v. sol. alcohol and ether.

Reactions.—1. *Sodium amalgam* reduces it to succinic acid.—2. *Boiling water* converts the sodium salt into hydro-sodic bromo-malate, the Ba salt into hydro-baric bromo-maleate and barium racemate, the silver salt into inactive tartaric acid, and the acid itself into HBr and bromo-maleïc acid.—3. *Water* at 140° gives iso-bromo-maleïc acid.—4. NH_3 gives bromo-amido-succinic acid.—5. *Reduction* in acid solution gives fumaric acid (Ossipoff, *Bl.* [2] 34, 346).—6. Heating with *thio-urea* gives fumaric acid (Nencki a. Sieber, *J. pr.* [2] 25, 79).

Salts. — $(NH_4)_2A''$. — Na_2A'' 4aq. — Ag_2A''. — CaA'' 2aq.

Mono-methyl ether MeHA'': decomposes about 215°.—NaMeA'' 4aq (Claus, *B.* 15, 1844).

Mono-ethyl ether EtHA'' [275°]. — KEtA'' 1½aq. NaEtA'' 2aq.—AgEtA'' 1½aq (C.).

Methyl ether Me_2A''. [62°]. Mono-symmetrical crystals. Prepared by the action of bromine on methyl fumarate.

Ethyl ether Et_2A''. [58°]. (K.; A.); [68°] (Lehrfeld, *B.* 14, 1820). Rhombic crystals. Prepared by the action of bromine on ethyl fumarate. On heating to 170° it decomposes into bromo-maleïc ether and HBr (Anschütz, *B.* 12, 2281). Aniline converts it into $C_2H_2(NPhH)_2(CO_2Et)_2$ [145°] (Lopatine, *C. R.* 105, 230).

Methyl-ethyl ether MeEtA'' [63°] (C.).

Chloride $C_4H_2Br_2O_2Cl_2$ [63°]. From Br and succinyl chloride or fumaryl chloride (Perkin a. Duppa, *C. J.* 13, 102; K.).

Amic acid $CO_2H.C_2H_2Br_2.CO.NH_2$. Unstable crystals (C.; Michael a. Wing, *Am.* 6, 421).

Anilide (?) NHPh.CO.CHBr.CHBr.CO.NHPh. From the anilide of fumaric acid and bromine (Anschütz a. Wirtz, *A.* 239, 138; *Am.* 9, 240). White powder, does not melt below 300°.

Phenyl-imide NPh:(C_2O_2):$C_2H_2Br_2$. [159°]. From the phenyl-imide of maleïc acid (maleanil) in chloroform by adding Br (A. a. W.).

Iso- (or *allo*) di-bromo-succinic acid

$$CO_2H.CH_2.CBr_2.CO_2H \text{ or } \left\langle\begin{matrix} CHBr—C(OH)_2 \\ \quad\quad\quad >O \\ CHBr—CO \end{matrix}\right.$$

(*cf.* Anschütz, *A.* 239, 181). [160°].

Formation.—1. From maleïc acid and Br (Kekulé, *A. Suppl.* 2, 89).—2. Together with its isomeride, by heating bromo-maleïc anhydride with HBr, or succinic acid with water and Br at 140° (Franchimont, *B.* 6, 199; Bourgoin, *B.* 6. 624).—3. From (δ)-bromo-pyromucic acid, Br. and water (Hill a. Sanger, *A.* 232, 53).

Preparation.—By dissolving its anhydride in water (Pictet, *B.* 13, 1670).

Properties.—Large crystals; more soluble in water than its isomeride. At 180° it gives off HBr, bromo-fumaric acid being formed.

Reactions.—1. Boiling *water* converts the acid and its Ba salt into bromo-maleïc acid, but the Ag salt into racemic acid.—2. Moist Ag_2O gives pyruvic acid (Beilstein a. Wiegand, *B.* 15, 1499).—3. *Sodium amalgam* produces succinic acid.

The Di-methyl ether $A''Me_2$ and the *Di-ethyl-ether* $A''Et_2$ are oily liquids, insol. water (Pictet, *B.* 13, 1670).

Anhydride $C_2H_2Br_2.C_2O_3$ [32°]. Prepared by heating maleïc anhydride with bromine at 100° (Pictet, *B.* 13, 1669). Colourless tables. Has a great affinity for water, with which it forms iso-dibromo-succinic acid. On heating to 100° it evolves HBr forming bromo-maleïc anhydride.

Tri-bromo-succinic acid

$CO_2H.CBr_2.CHBr.CO_2H$. [137°]. From bromo-maleïc or bromo-fumaric acid and Br (Petri, *A.* 195, 69). Deliquescent needles; boiling water converts it into di-bromo-acrylic acid.

BROMO-SULPHI-BENZOIC ACID

$C_6H_3Br(SO_2H)(CO_2H)$ [4:2 or 3:1]. [238°-245°]. From $C_6H_3Br(SO_2Cl)CO_2H$ by treatment with alcohol and zinc-dust (C. Böttinger, *A.* 191, 24).—BaA''.—$BaH_2A''_2$ 2aq.—$CaH_2A''_2$ 8aq.

BROMO-SULPHI-BENZOIC ALDEHYDE

$C_6H_3Br(SO_2H)CHO$. [131°]. One of the products got by reducing, by zinc-dust and alcohol, the mixture of chlorides got by acting on $C_6H_3Br(SO_3Na)(CO_2Na)$ by PCl_5. It is formed from $C_6H_3Br(SO_2Cl)(COCl)$ present in the mixture. Salt.—BaA'_2 5aq.

BROMO-SULPHO-BENZOIC ACID

$C_6H_3Br(SO_3H)(CO_2H)$ [2:3 or 5:1]. From the corresponding bromo-toluene sulphonic acid by chromic mixture (Retschy, *A.* 169, 45).—KHA'' ½aq.—BaA'' 2aq.—PbA'' 2aq.

Bromo-sulpho-benzoic acid

$C_6H_3Br(SO_3H)(CO_2H)$ [1:3:5]. From *m*-bromo-benzoic acid and SO_3 (Hübner a. Upmann, *Z.* [2] 6, 295; Roeters van Lennen, *Z.* [2] 7, 67; Böttinger, *B.* 7, 1779). Delicate deliquescent needles. Potash-fusion converts it into *s*-di-oxy-benzoic acid.

Salts.—$NaHA''$. — Ag_2A''. — CaA'' 1½aq.—BaA'' 2½aq.—$BaHA''_2$ aq.—CuA''.

Bromo-sulpho-benzoic acid

$C_6H_3Br(SO_3H)(CO_2H)$ [4:2:1]. From bromo-toluene *o*-sulphonic acid by chromic mixture (Weiss, *A.* 169, 26).—KHA''.—CaA''.—BaA'': V. sol. water.

Imide $C_6H_3Br<\substack{SO_2\\CO}>NH$. *Bromo-benzoic sulphinide.* [217°]. From (4, 1, 2)-bromo-toluene sulphamide and $KMnO_4$. Also from the acid K salt by successive treatment with PCl_5 and NH_3 (Remsen a. Bayley, *Am.* 8, 229). Long needles (from water); v. sol. alcohol and hot water, v. sl. sol. HClAq. Sublimes at 200°. Its taste is extremely sweet at first and then extremely bitter. — $Ba(C_7H_3BrNSO_3)_2$ 7½aq. — $Ca(C_7H_3BrNSO_3)_2$ 7½aq. — $AgC_7H_3BrNSO_3$. — $C_2H_5(C_7H_3BrNSO_3)$: [199°]; formed by successive treatment with PCl_5 and alcohol.

Bromo-sulpho-benzoic acid

$C_6H_3Br(SO_3H)(CO_2H)$ [4:3:1]. Formed by oxidation of the corresponding bromo-toluene sulphonic acid (Hässelbarth, *A.* 169, 12).—KHA'' aq.—BaA'' ½aq.—PbA'' 2aq.

Bromo-sulpho-benzoic acid

$C_6H_3Br(SO_3H)(CO_2H)$ [4: 2 or 3 :1]. Probably identical with the preceding. From *p*-bromo-benzoic acid and fuming H_2SO_4 heated for 8 hours at 130° (Böttinger, *A.* 191, 13). Matted needles, v. sl. water.

Salts.—$NaHA''$ 2aq.—Ag_2A'' 3aq.—BaA'' 3aq.—$BaH_2A''_2$ 4aq.—CuA'' 3aq.—PbA'' 7aq.

Chloride $C_6H_3Br(SO_2Cl)CO_2H$. [197°] (with decomposition). Needles (from ether). M. sol. cold ether, which separates it from another chloride.

Acid ether $C_6H_3Br(SO_3Et)(CO_2H)$. [84°]. From the chloride and alcohol.

Amic acid $C_6H_3Br(SO_2NH_2)CO_2H$. [230°].—BaA'_2 12aq.

Amic acid $C_6H_3Br(SO_3H)CONH_2$. [262°].

Amic ether $C_6H_3Br(SO_3Et)(CONH_2)$ [128°].

Bromo-di-sulpho-benzoic acid

$C_6H_2Br(SO_3H)_2CO_2H$. From *p*-bromo-toluene disulphonic acid and boiling fuming HNO_3 (Kornatzki, *A.* 221, 196). — K_3A'''aq.—$Ba_3A'''_2$12aq.

Chloride. [151°]. Trimetric tables from ether).

Amide. [above 260°]. Small prisms in stars.

BROMO - SULPHO - PHENYL - PROPIONIC ACID $C_9H_9BrSO_5$ *i.e.*

[4:3:1] $C_6H_3Br(SO_3H).CH_2.CH_2.CO_2H$. Prepared by the action of fuming sulphuric acid on *p*-bromo-phenyl-propionic acid (Göring, *C. C.* 1877, 793, 808). Non-deliquescent rhombic plates (containing 2½aq). $a:b:c = 1{\cdot}3013:1:0{\cdot}7831$.

Salts. — $NaHA''$ 3aq. — BaA'' 2aq.—$H_2BaA''_2$ 8aq; triclinic crystals: $a:b:c = 0{\cdot}4941:1:0{\cdot}5046$; $\alpha = 68°\ 36'$; $\beta = 98°\ 22'$; $\gamma = 83°\ 38'$. — CaA'' 3aq. — $CaH_2A''_2$ 8aq: monoclinic crystals: $a:b:c = 0{\cdot}7062:1:0{\cdot}9774$; $\beta = 86°\ 45'$.

DI-BROMO-SULPHO-PYROMUCIC ACID

$$\begin{array}{l}CBr=C-CO_2H\\ \mid \qquad\quad >O\\ CBr=C-SO_3H\end{array}$$

Di-bromo-sulpho-furfurane-carboxylic acid. Formed by sulphonation of di-bromo-pyromucic acid [192°] with fuming H_2SO_4. By the action of bromine upon its barium salt, di-bromo-maleïc acid is formed. By zinc-dust and aqueous NH_3 it is de-brominated, yielding sulpho-pyromucic acid. $A''Ba$ 5aq: easily soluble long fine needles (Hill a. Palmer, *B.* 18, 2096).

BROMO-SULPHYDRO-BENZOIC ACID

$C_6H_3Br(SH)CO_2H(?)$ [256°] (U.); [243°] (L.). From the chloride of sulphonated *m*-bromo-benzoic acid by tin and HCl (Upmann, *Z.* 1870, 295; Van Lennen, *Z.* 1871, 67). Needles, insol. water. Reduced by sodium-amalgam to $C_6H_4(SH)CO_2H$. Iodine converts its Na salt into an acid [130°].

Salts.—ZnA'_2.—PbA'_2.—BaA'_2.

Bromo-sulphydro-benzoic acid

$C_6H_3Br(SH)CO_2H$. [194°]. From the chloride of (1, 3, 5)-bromo-sulpho-benzoic acid by tin and HCl (Frerichs, *B.* 7, 795). Laminæ.—PbA'_2 3aq.

BROMO-TEREPHTHALIC ACID

$C_6H_3Br(CO_2H)_2$ [2:1:4]. [306° cor.]. Needles

containing aq (Fis.) or anhydrous (Fil.). Prepared by oxidation of bromo-toluic acid with $KMnO_4$ (Fischli, *B.* 12, 619), by oxidation of bromo-cymene (Fileti, *G.* 16, 286), or of *p*-phenyl-toluene [129°] (Carnelley a. Thomson, *C. J.* 51, 88). It gives a sublimate of anhydride) [245°].

Salts.—K_2A'': needles.—Ag_2A'' aq. White insoluble flocculent pp.—$A''Cu$: light blue pp.

Chloride $C_6H_3Br(COCl)_2$. (305° cor.).

Amide $C_6H_3Br(CONH_2)_2$. [270°]: insoluble needles.

Methyl ether $C_6H_3Br(CO.OEt)_2$. [42°] (Fis.); [52°] (Fil.). (above 300°). Needles.

Di-bromo-terephthalic acid $C_6H_2Br_2(CO_2H)_2$ [6:3:4:1]. Formed by oxidation of di-bromo-*p*-toluic acid [195°] with $KMnO_4$ (Schultz, *B.* 18, 1762) or of di-bromo-cymene with dilute HNO_3 (Claus a. Wimmel, *B.* 13, 902). Laminæ (from HOAc); does not melt below 320°.

Salts.— $A''Ca\,4aq$: easily soluble microscopic needles. — $A''Ba\,2aq$ and $A''Ba\,5aq$: microscopic needles.

Ethyl ether $A''Et_2$. [121°]. (c. 335°). Pearly plates.

***o*-Di-bromo-terephthalic acid.**

Hexa-hydride $C_6H_8Br_2(CO_2H)_2$ [2:3:1:4]. *Di-o-bromo-hexa-hydro-benzene-di-p-carboxylic acid.* Formed by direct combination of tetra-hydro-terephthalic acid with Br in the cold. Granular crystals (containing aq). Nearly insol. cold water, sparingly in hot. By Ag_2O it is converted into an acid (probably $C_6H_8(OH)_2(CO_2H)_2$) which by treatment with bromine yields tetra-bromo-pyrocatechin (Baeyer, *B.* 19, 1808).

DI-BROMO-TETRADECANE $C_{14}H_{28}Br_2$. *Tetradecylene bromide.* [0°]. Colourless liquid. Formed by addition of Br to tetradecylene (Krafft, *B.* 17, 1372).

HEXA-BROMO-DITHIËNYL $\begin{matrix} C_4Br_3S \\ | \\ C_4Br_3S \end{matrix}$. [255° uncor.]. Formed by heating an acetic acid solution of dithiënyl with an excess of bromine (Nahnsen, *B.* 17, 2198). Small needles. V. sol. hot benzene, v. sl. sol. cold benzene and hot alcohol.

TRI-ω-BROMO-DI-THIËNYL-ETHANE $CBr_3.CH(C_4H_3S)_2$. [102°]. Obtained by adding H_2SO_4 to a mixture of thiophene and bromal dissolved in acetic acid. Small pyramids. V. sol. ether, CS_2, and hot alcohol. With isatin and H_2SO_4 it gives a violet-red colour (Peter, *B.* 17, 1344).

DI-ω-BROMO-DI-THIËNYL-ETHYLENE $CBr_2{:}C(C_4H_3S)_2$. Formed by boiling tri-bromo-di thiënyl-ethane with alcoholic KOH, or better KCN (Peter, *B.* 17, 1344). Colourless oil. Volatile with steam. Gives a violet-red colour with isatin and H_2SO_4.

BROMO-THIËNYL METHYL KETONE $C_4SH_2Br.CO.CH_3$. *Bromo-acetothiënone.* [94°]. Formed by the action of acetyl chloride upon mono- or di-bromo-thiophene in presence of Al_2Cl_6. Stout colourless needles. Sol. hot alcohol, less in cold. Very volatile with steam. By alkaline $KMnO_4$ it is oxidised to bromo-thiophene-carboxylic acid [140°].

Phenyl hydrazide $C_4SH_2Br.C(N_2HPh).CH_3$: [122°]; tables; sl. sol. alcohol (Gattermann a. Römer, *B.* 19, 689).

BROMO-THIO-CRESOL *v.* BROMO-TOLYL MERCAPTAN.

DI-BROMO-THIOHYDANTOÏN $C_3H_2ON_2SBr_2$. Formed by the action of bromine on a solution of thiohydantoïn in aqueous HCl (Mulder, *B.* 8, 1263; Kramps, *B.* 13, 789). Colourless crystals. Insol. cold water, sol. alcohol and ether. Decomposed by hot water.

BROMO-THIO-OXY-BENZOIC ACID *v.* BROMO-SULPHYDRO-BENZOIC ACID.

(α)-BROMO-THIOPHENE C_4SH_3Br. '*β*'-*Bromo-thiophene.* (150°). S.G. $\frac{23}{23}$ 1·652. Colourless liquid. Formed by bromination of thiophene (Meyer, *B.* 16, 1472). Isolated from the crude di-bromo-thiophene obtained by fractional bromination of benzene that contains thiophene. By EtBr and Na it is converted into '*β*'-ethyl-thiophene (Schleicher, *B.* 18, 3015).

Di-bromo-thiophene $C_4SH_2Br_2$. (211° cor.). S.G. $\frac{23}{23}$ 2·147. Colourless oil. Formed by dropping bromine into thiophene cooled with water. Prepared by fractional bromination of benzene that contains thiophene. With isatin and H_2SO_4 it gives a deep-blue colour (Meyer, *B.* 16, 1469; Meyer a. Stadler, *B.* 18, 1488).

Tri-bromo-thiophene C_4SHBr_3. [29°]. (260° cor.). Formed by further bromination of di-bromothiophene. Long white glistening crystals. V. sol. hot alcohol and ether, sl. sol. cold alcohol. Gives the indophenine reaction. By sulphonation and debromination it yields thiophene-(*β*)-sulphonic acid (Rosenberg, *B.* 18, 1773).

Tetra-bromo-thiophene C_4SBr_4. [112°]. (326° cor.). Long white needles. Formed by further bromination of di-bromo-thiophene (Meyer a. Kreis, *B.* 16, 2172).

BROMO-THIOPHENE-CARBOXYLIC ACID $C_4SH_2Br(CO_2H)$. [140°]. Formed by oxidation of bromo-thiënyl methyl ketone with alkaline $KMnO_4$. Colourless glistening needles (from water). Sublimes in pearly spikes. M. sol. hot water, nearly insol. cold water (Gattermann a. Römer, *B.* 19, 690).

Di-bromo-thiophene-(α)-carboxylic acid $C_4SHBr_2.CO_2H$. *Di-bromo-thiophenic acid.* [222°]. Obtained by bromination of (α)-thiophene-carboxylic acid (*q.v.*). White monoclinic needles. Sublimes on heating. V. sol. alcohol and ether, sl. sol. hot water, insol. cold water. Sparingly volatile with steam. Isatin and H_2SO_4 yield a dirty-green colouration quickly becoming brown. A solution of the ammonium salt gives white pps. with $AgNO_3$, $Pb(OAc)_2$, $HgNO_3$, and $SnCl_2$; yellow pp. with Fe_2Cl_6; and greenish-white pp. with $CuSO_4$.

Salts.—$A'Ag$: white curdy pp. becoming crystalline. — $A'K$: easily soluble crystals. — $A'_2Ba\,3\frac{1}{2}aq$: white needles, v. sol. hot water, sl. sol. cold.

Chloride $C_4SHBr_2.COCl$: (250°–270°); silky needles.

Amide $C_4SHBr_2.CONH_2$: [167°]; fine white felted needles; v. sol. alcohol and ether, sparingly in hot water.

Methyl ether $C_4SHBr_2.CO_2Me$: [80°]; white needles (Peter, *B.* 18, 543; Bonz, *B.* 18, 2308).

DI-BROMO-THIOPHENE-SULPHONIC ACID $C_4HBr_2S.SO_3H$. Formed by sulphonating di-bromo-thiophene. By sodium-amalgam it is

reduced to thiophene-'β'-sulphonic acid.—PbA'_2 $5\frac{1}{2}$aq: small crystals, sol. hot water.

Chloride $C_4HBr_2S.SO_2Cl$: [33°].

Amide $C_4HBr_2S.SO_2NH_2$: [147°]; felted needles; sparingly soluble in water (Langer, *B.* 17, 1566; 18, 553; Rosenberg, *B.* 18, 3030).

Di-bromo-thiophene-di-sulphonic acid $C_4SBr_2(SO_3H)_2$. Obtained by boiling the anhydride with alkalis. It very readily splits off H_2O with conversion into the anhydride.

Salts.—Na_2A'' 3aq: very soluble silky needles.—$(NH_4)_2A''$ aq.—PbA'': plates, sol. hot water.—BaA'' aq: sparingly soluble white glistening spikes.

Anhydride $C_4SBr_2<\begin{smallmatrix}SO_2\\SO_2\end{smallmatrix}>O$: white glistening plates, v. sol. alcohol and benzene, insol. water and ligroïn. Obtained by the action of fuming sulphuric acid (4 vols.) on di-bromo-thiophene (1 vol.).

Chloride $C_4SBr_2(SO_2Cl)_2$: [220°]; glistening white needles; sol. ether.

Amide $C_4SBr_2(SO_2NH_2)_2$: [c. 270°]; crystalline powder; nearly insol. water (Langer, *B.* 17, 1569; 18, 554; Rosenberg, *B.* 18, 3030).

Tri-bromo-thiophene-sulphonic acid $C_4SBr_3(SO_3H)$. Formed together with the anhydride by sulphonation of tri-bromo-thiophene [29°].—BaA'_2 aq: sparingly soluble white warty crystals.

Anhydride $(C_4SBr_3.SO_2)_2O$: [116°]; volatile with steam; white solid; v. sol. alcohol and ether, v. sl. sol. water.

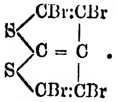
Chloride $C_4SBr_3(SO_2Cl)$: [126°]; needles.

Amide $C_4SBr_3(SO_2NH_2)$: needles (from water) (Rosenberg, *B.* 18, 1774, 3028).

DI-BROMO-THIOPHENIC ACID *v.* DI-BROMO-THIOPHENE-CARBOXYLIC ACID.

BROMO-THIO-PHENOL *v.* BROMO-PHENYL MERCAPTAN.

TETRA-BROMO-THIOPHTHENE $C_6S_2Br_4$ *i.e.*



[172°]. Formed by bromination of thiophthene. Long white needles (from benzene). V. sol. hot benzene, sl. sol. alcohol (Biedermann a. Jacobsen, *B.* 19, 2447).

BROMO-THIOTOLENE *v.* BROMO-METHYL-THIOPHENE.

BROMO-THIOXENE *v.* BROMO-DI-METHYL-THIOPHENE.

***m*-BROMO-THYMOHYDROQUINONE** $C_6HMePrBr(OH)_2$ [1:4:5:3:6]. [53°]. Formed by the action of conc. HBr upon thymoquinone at a low temperature. Colourless needles (Schniter, *B.* 20, 1318). Formed also by reduction of the corresponding quinone with SO_2 (Mazzara a. Discalzo, *G.* 16, 195). Changes spontaneously to a substance melting at 37° (M. a. D.).

Di-acetyl derivative $C_6HMePrBr(OAc)_2$. [91°]. From thymoquinone and AcBr (Schulz, *B.* 15, 657).

Di-bromo-thymo-hydroquinone

Di-acetyl derivative $C_6MePrBr_2(OAc)_2$. [122°]. From di-acetyl bromo-thymo-hydroquinone and Br (S.).

BROMO-THYMOLS and their ethyl derivatives appear to have been obtained by Paterno a. Canzoneri, *G.* 10, 233, Armstrong a. Thorpe, *Brit. Assoc. Reports*, 1875, 112; and Lallemand, *A. Ch.* [3] 49, 148.

BROMO-THYMOL SULPHONIC ACID $C_{10}H_{13}BrSO_4$ *i.e.* $C_6HMePrBr(OH)(SO_3H)$. From potassium thymol (α)-sulphonic acid and Br.—KA' $1\frac{1}{2}$aq.—BaA'_2 (Engelhardt a. Latschinoff, *Z.* 1871, 261).

***m*-BROMO-THYMOQUINONE** $C_6HMePrBrO_2$ [1:4:5:3:6]. [48°] (M. a. D.); [45°] (S.). Formed by oxidation of the corresponding bromo-thymo-hydroquinone with Fe_2Cl_6. Glistening yellow plates (Schniter, *B.* 20, 1318). From bromo-amido-thymol and nitrous acid (Mazzara a. Discalzo, *G.* 16, 195). A crystalline bromo-thymoquinone was got by Carstanjen (*J. pr.* [2] 3, 55) in brominating thymoquinone. Andresen (*J. pr.* [2] 23, 184) obtained a liquid isomeride by brominating thymoquinone chloro-imide.

Di-bromo-thymo-quinone $C_6Br_2MePrO_2$. [74°]. The ethereal extract from the product of the action of HBr on thymo-quinone-chloro-imide (*q. v.*) is evaporated and the residue distilled with steam (Andresen, *J. pr.* [2] 23, 184). From thymoquinone and Br (C.). Lemon-yellow plates (by adding water to the alcoholic solution).

***o*-BROMO-TOLUENE** C_7H_7Br *i.e.* C_6H_4MeBr [1:2]. (182°). S.G. $\frac{18.2}{4}$ 1·2031. S.V. 141·95 (Schiff, *B.* 19, 564).

Formation.—1. Together with *p*-bromo-toluene, by brominating cold toluene, in the dark, in daylight, or with addition of iodine (Hübner a. Wallach, *Z.* [2] 5, 22, 138, 499; *A.* 154, 293; Dmochowsky, *B.* 5, 333; Kekulé, *A.* 137, 192; Beilstein, *A.* 143, 369; Cannizzaro, *A.* 141, 198; Glinzer a. Fittig, *A.* 133, 47; 136, 301; Fittig, *A.* 147, 39; Rosenstiehl a. Nikiforoff, *Z.* [2] 5, 635; Hübner a. Retschy, *Z.* [2] 7, 618; Lauth a. Grimaux, *Bl.* 1866, i, 347; 1867, i, 108; Körner, *G.* 4; Hübner a. Jannasch, *A.* 170, 117; Louguinine, *B.* 4, 514; Reyman, *Bl.* [2] 26, 533; Schramm, *B.* 18, 607).—2. From *o*-toluidine by the diazo- reaction (Wroblewsky, *A.* 168, 171; Jackson, *Am.* 1, 93).—3. Together with naphthalene, by the action of (α)-bromo-naphthalene on toluene in presence of Al_2Cl_6 (Roux, *Bl.* [2] 45, 520).

Properties.—Oil.

Reactions.—1. Converted by dilute HNO_3 into *o*-bromo-benzoic acid (Zincke, *B.* 7, 1502).—2. *Sodium* has no action at 15°.—3. *Sodium* and MeI form *o*-xylene.—4. The *copper-zinc couple* has no action (Gladstone a. Tribe, *C. J.* 47, 448).

***m*-Bromo-toluene** C_6H_4MeBr [1:3]. (184°). S.G. $\frac{18}{}$ 1·401 (W.).

Formation.—1. From $C_6H_3MeBr(NH_2)$ [1:3:4] by the diazo- reaction (Wroblewsky, *Z.* [2] 7, 609; *A.* 168, 155; Grete, *A.* 177, 231).—2. From the same bromo-*p*-toluidine by successive conversion into $C_6H_2(NO_2)MeBr(NH_2)$ [5:1:3:4], $C_6H_3(NO_2)MeBr$ [5:1:3], $C_6H_4(NH_2)Me$ [5:1], and C_6H_4BrMe [5:1] (Wroblewsky, *A.* 192, 206).

Properties.—Liquid, even at −20°. Oxidised by chromic mixture to *m*-bromo-benzoic acid.

***p*-Bromo-toluene** C_6H_4MeBr [1:4]. [28·5°]. (185° i. V.) (Hübner a. Post, *A.* 169, 6). S.G. $\frac{22}{4}$ 1·411 (Kekulé, *A.* 137, 192).

Formation.—Together with *o*-bromo-toluene (*q. v.*) by brominating toluene.

Properties.—Trimetric crystals.

Reactions.—1. CrO_3 forms *p*-bromo-benzoic acid.—2. *Sodium* even at 15° forms ditolyl (Zincke, *B.* 4, 396; Louguinine, *B.* 4, 514).—3. *Sodium* and MeI gives *p*-xylene.—4. The *copper-zinc couple* has no action (G. a. T.).—5. Taken internally, it is excreted as *p*-bromo-benzoic and *p*-bromo-hippuric acids (Preusse, *H.* 5, 63).—6. CrO_2Cl_2 forms $C_6H_4Br.CH(O.CrOCl)_2$ (Etard, *A. Ch.* [5] 22, 241).

ω-**Bromo-toluene** *v.* Benzyl bromide.

Di-bromo-toluene $C_6H_3MeBr_2$ [1:2:3]. [28°]. From $C_6H_2(CH_3)(NH_2)Br_2$ [86°] by displacing NH_2 by H (Nevile a. Winther, *C. J.* 37, 431). Gives on oxidation with HNO_3 di-bromo-benzoic acid [146°–148°]. On nitration it gives a mono-nitro- derivative [57°] which reduces to an amido- compound [53°].

Di-bromo-toluene $C_6H_3MeBr_2$ [1:2:4]. From di-bromo-*m*-toluidine [75°] by eliminating NH_2. Also from $C_6H_3(CH_3)(NH_2)Br$ [1:2:4] by diazo-perbromide reaction. Oil. On nitration gives di-bromo-nitro-toluene [80°]. On oxidation with HNO_3 gives di-bromo-benzoic acid [169°].

Di-bromo-toluene $C_6H_3MeBr_2$ [1:2:5]. (236°). S.G. $\frac{18}{}$ 1·813. Formed by brominating toluene (Wroblewsky, *Z.* [2] 6, 239). From acetyl-*o*-toluidine by brominating, saponifying, and displacing NH_2 by Br by the diazo- reaction (N. a. W.). Also from acetyl-*m*-toluidine in the same way. Thus $C_6H_3(CH_3)(NH_2)Br$ [1:2:5] and $C_6H_3(CH_3)Br(NH_2)$ [1:2:5] give the same $C_6H_3(CH_3)Br_2$. Oil. On nitration it gives a nitro- compound [88°], which reduces to an amido- compound [85°]. Oxidised by dilute HNO_3, it gives di-bromo-benzoic acid [149°–153°]; this distilled with lime gives a solid, [86°], probably *p*-di-bromo-benzene.

Di-bromo-toluene $C_6H_3MeBr_2$ [1:2:6]. (246°). S.G. $\frac{22}{}$ 1·812. From di-bromo-*m*-toluidine [35°] (Wr.; N. a. W.) or from di-bromo-*p*-toluidine [88°] by diazo- reaction. Oil. On nitration it gives two nitro- compounds, [161°], and [c. 80°]. On oxidation it gives di-bromo-benzoic acid [150°–167°].

Di-bromo-toluene $C_6H_3MeBr_2$ [1:3:4]. (241°). S.G. $\frac{19}{}$ 1·812. Formed in brominating toluene containing iodine in sunlight (Jannasch, *A.* 176, 286). Also from bromo-*p*-toluidine by the diazo-perbromide reaction (N. a. W.; Wr.). Oil. Gives a nitro- derivative, [87°], reducing to an amido-derivative [98°]. By oxidation with CrO_3 it gives di-bromo-benzoic acid [233°].

Di-bromo-toluene $C_6H_3MeBr_2$ [1:3:5]. [39°]. (246°). From $C_6H_2(CH_3)(NH_2)Br_2$ [73°] and its isomeride [46°] (N. a. W.; Wr.). With HNO_3 it gives two di-nitro- compounds, [158°] and [105°]. On oxidation with CrO_3 it gives di-bromo-benzoic acid [208°–210°].

Di-bromo-toluene $C_6H_3MeBr_2$. [108°]. The existence of this body, said to be formed in brominating toluene (Fittig, *A.* 147, 39), is called in question by Nevile and Winther.

Other **Di-bromo-toluenes** are described as Benzylidene bromide and Bromo-benzyl bromide.

Tri-bromo-toluene $C_6H_2MeBr_3$ [1:2:3:4]. [44°]. From $C_6H(CH_3)(NH_2)Br_3$, [97°], by nitrous gas (Nevile a. Winther, *C. J.* 37, 447). On nitration it gives a nitro- compound [107°].

Tri-bromo-toluene $C_6H_2MeBr_3$ [1:2:3:5]. [53°]. From di-bromo-*o*-toluidine [46°] by diazo-perbromide reaction (N. a. W.). Long flat needles.

Tri-bromo-toluene $C_6H_2MeBr_3$ [1:2:5:6]. [59°]. From [1:3:2:5:6] $C_6H(CH_3)(NH_2)Br_3$ [94°] by nitrous gas. On nitration it gives a nitro- compound [91°].

Tri-bromo-toluene $C_6H_2MeBr_3$ [1:2:4:6]. [66°]. (290°). From tri-bromo-*m*-toluidine [101°] by nitrous gas (N. a. W.; Wroblewsky, *A.* 168, 194). On nitration it gives a di-nitro- compound [c. 220°].

Tri-bromo-toluene $C_6H_2MeBr_3$ [1:3:4:5]. [89°]. From di-bromo-*p*-toluidine by diazo-perbromide reaction (N. a. W.).

Tri-bromo-toluene $C_6H_2MeBr_3$ [1:3:4:6]. [112°]. From di-bromo-*m*-toluidine [75°] and from di-bromo-toluidine [85°] by diazo-perbromide reaction (N. a. W.).

Tri-bromo-toluene ? [150°]. Formed by heating potassium tri-bromo-phenol with KOAc (Pfankuch, *J. pr.* [2] 6, 103).

Tetra-bromo-toluene C_6HMeBr_4 [1:2:3:4:6]. [105°–108°]. From tetra-bromo-*m*-toluidine [224°] by alcohol and nitrous gas. Also from tri-bromo-*m*-toluidine [100°] by diazo-perbromide reaction (Nevile a. Winther, *C. J.* 37, 449). Fuming HNO_3 forms the nitro- compound [216°].

Tetra-bromo-toluene C_6HMeBr_4 [1:3:4:5:6]. [111°]. From tri-bromo-*m*-toluidine [96°], by diazo-perbromide reaction (N. a. W.). Its nitro-compound melts at [212°].

Tetra-bromo-toluene C_6HMeBr_4 [1:2:3:5:6]. [117°]. From tri-bromo-*m*-toluidine [94°] by diazo-perbromide reaction. Its nitro- derivative melts at [213°].

Penta-bromo-toluene C_6MeBr_5. [285°]. From tetra-bromo-*m*-toluidine by diazo-perbromide reaction (Nevile a. Winther, *C. J.* 37, 450). From toluene Al_2Br_6, and Br at 0° (Gustavson, *Bl.* [2] 28, 347; *B.* 10, 971). Long needles (from benzene).

***o*-BROMO-TOLUENE SULPHONIC ACID** $C_7H_7BrSO_3$ *i.e.* $C_6H_3MeBr(SO_3H)$ [1:2:5?]. From *o*-bromo-toluene by sulphonation (Hübner a. Post, *A.* 169, 31; *cf.* Dmochowsky, *B.* 5, 333). Also from brominated (1, 4, 3)-*p*-toluidine sulphonic acid by displacement of NH_2 by H (Pechmann, *A.* 173, 212). Reduced by sodium-amalgam to toluene *m*-sulphonic acid.

Salts.—KA′ ½aq.—NaA′ ½aq.—BaA′$_2$ 2aq.—BaA′$_2$ 5½aq. S. (of BaA′$_2$) ·35 at 14°.—PbA′$_2$ 2aq. S. (of PbA′$_2$) ·52 at 18°.—PbA′$_2$ 3aq.

Chloride $C_6H_3MeBr(SO_2Cl)$. [53°].

Amide $C_6H_3MeBr(SO_2NH_2)$. [134°].

o-**Bromo-toluene sulphonic acid** $C_6H_3MeBr(SO_3H)$ [1:2:5]. From *o*-toluidine by sulphonating and displacing NH_2 by Br (Pagel, *A.* 176, 294; Nevile a. Winther, *B.* 13, 1943; *cf.* Gerver, *A.* 169, 381). Reduced by sodium-amalgam to toluene *m*-sulphonic acid.

Salts.—KA′aq.—CaA′$_2$ aq.—BaA′$_2$ ½aq. S. 1·2 at 25° (P.).—BaA′$_2$ 2½aq.—BaA′$_2$ 9aq. S. 8·9 at 17·5° (G.).—PbA′$_2$ 2aq.—CuA′$_2$ 3aq.

Chloride [53°] (P.); [56°] (N. a. W.).

Amide [c. 135°] (P.); [147°] (N. a. W.).

This acid is probably identical with the preceding.

o-**Bromo-toluene sulphonic acid** $C_6H_3MeBr(SO_3H)$ [1:2:4]. From *o*-toluidine *p*-sulphonic acid by the diazo- reaction (Hayduck,

A. 172, 206).—KA': nodules of minute needles.—BaA'_2 2aq.—PbA'_2 $2\frac{1}{2}$aq.

Chloride $C_6H_3MeBr(SO_2Cl)$. [54°].

Amide $C_6H_3MeBr(SO_2NH_2)$. [151°].

Bromo-toluene sulphonic acid $C_6H_3MeBrSO_3H$ [1:3:5]. From bromo-*o*-toluidine sulphonic acid or from bromo-*p*-toluidine sulphonic acid by displacement of NH_2 by H. Potash-fusion gives orcin (Nevile a. Winther, *B.* 13, 1944; *C. J.* 41, 420).

Chloride $C_6H_3MeBr.SO_2Cl$. [52°].

Amide $C_6H_3MeBr.SO_2NH_2$. [139°].

***m*-Bromo-toluene sulphonic acid** $C_6H_3MeBr(SO_3H)$. Formed by sulphonating *m*-bromo-toluene (Grete, *B.* 7, 795; 8, 565; *A.* 177, 233).—BaA'_2 aq.—SrA'_2 aq.—CaA'_2 2aq.—MgA'_2 6aq.—CuA'_2 4aq.—PbA'_2 3aq. According to Wroblewsky (*A.* 168, 166; *Z.* [2] 7, 6) three bromo-toluene sulphonic acids are formed by sulphonating *m*-bromo-toluene, the Ba salts being BaA'_2 aq. S. ·528, BaA'_2 3aq. S. 1·452, and BaA'_2 $2\frac{1}{2}$aq. S. 5·248 at 19°; Grete, however, could only obtain the acid just described.

Bromo-toluene *o*-sulphonic acid $C_6H_3MeBr(SO_3H)$. From (1, 4, 2)-toluidine sulphonic acid by bromination and elimination of NH_2 (Weckwarth, *A.* 172, 196).—NaA' $\frac{1}{2}$aq.—KA'aq.—BaA'_2 $2\frac{1}{2}$aq.—SrA'_2 $2\frac{1}{2}$aq.—PbA'_2 $3\frac{1}{2}$aq.—CuA'_2 $\frac{1}{2}$aq.

Chloride $C_6H_3MeBr(SO_2Cl)$: crystalline at −20°.

Amide $C_6H_3MeBr(SO_2NH_2)$: [c. 164°]; needles.

Bromo-toluene sulphonic acid $C_6H_3MeBr(SO_3H)$. From toluene by sulphonation, nitration, reduction, and displacement of NH_2 by Br (Weckwarth, *A.* 172, 193; Hayduck, *A.* 177, 57).—BaA'_2aq.

Chloride. Oil, slowly solidifying.

Amide. Does not melt below 230°.

***p*-Bromo-toluene *m*-sulphonic acid** $C_6H_3MeBr(SO_3H)$ [1:4:3]. [c. 108°]. From *p*-toluidine *m*-sulphonic acid by exchange of NH_2 for Br. Formed also in sulphonating *p*-bromo-toluene (E. Richter, *A.* 230, 319; Post a. Retschy, *A.* 169, 7; v. Pechmann, *A.* 173, 208; Nevile a. Winther, *C. J.* 37, 631). Laminæ (containing aq).—BaA'_2 7aq.—SrA'_2 7aq.—PbA'_2 3aq.

Chloride $C_6H_3MeBr(SO_2Cl)$. [61°].

Amide $C_6H_3MeBr(SO_2NH_2)$. [152°].

***p*-Bromo-toluene sulphonic acid** $C_6H_3MeBr(SO_3H)$ [1:4:2]. The chief product of the sulphonation of *p*-bromo-toluene (Hübner, *A.* 169, 6; Z. [2] 7, 618). Formed also from *p*-toluidine *o*-sulphonic acid by exchange of NH_2 for Br (Jenssen, *A.* 172, 237). Reduced by sodium-amalgam to toluene *o*-sulphonic acid.—NaA'_2aq.—CaA'_2 4aq.—BaA'_2 aq. S. ·53 at 8°.—SrA'_2aq.—PbA'_2 3aq.—CuA'_2 7aq.

Chloride $C_6H_3MeBr(SO_2Cl)$. [35°].

Amide $C_6H_3MeBr(SO_2NH_2)$. [167°].

***p*-Bromo-toluene ω-sulphonic acid** $C_6H_4Br.CH_2SO_3H$ [1:4]. *p-Bromo-benzyl sulphonic acid.* From *p*-bromo-benzyl bromide and K_2SO_3 (Jackson a. Hartshorn, *Am.* 5, 264). Also from $C_6H_4(NH_2).CH_2SO_3H$ by diazo- reaction (Mohr, *A.* 221, 222).—KA'. S. 6·2 at 18°.—CaA'_2.—BaA'_2 $1\frac{1}{2}$aq.—BaA'_2aq. S. (of BaA'_2) 67 at 18°.—PbA'_2. S. 2 at 18°.

Chloride. [107°] (M.); [115°] (J. a. H.).

Bromo-toluene disulphonic acid $C_6H_2MeBr(SO_3H)_2$ [1:2:3:5]. From $C_6H_2Me(NH_2)(SO_3H)_2$ by diazo- reaction (Limpricht, *B.* 18, 2177; Hasse, *A.* 230, 294).—K_2A'' 4aq.—BaA'' $1\frac{1}{2}$aq.

Chloride [90°].

Amide [238°].

***p*-Bromo-toluene disulphonic acid** $C_6H_2BrMe(SO_3H)_2$. From *p*-bromo-toluene, H_2SO_4 and SO_3 (Kornatzki, *A.* 221, 192). Cauliflower-like deliquescent crystals. Boiled for sixteen hours with conc. nitric acid it forms sulphuric acid $C_6H_2Br(CO_2H)(SO_3H)_2$, with $C_6H(NO_2)Br_2MeSO_3H$, and $C_6H_2(NO_2)Me(SO_3H)_2$.

Salts.—K_2A'' aq.—BaA'' 5aq.—PbA'' 2aq.

Chloride. [99°]. Trimetric plates (from ether).

Amide $C_6H_2MeBr(SO_2NH_2)_2$. [above 260°].

Bromo-toluene disulphonic acid $C_6H_2MeBr(SO_3H)_2$ [1:4:3:*x*]. Prepared from $C_6H_2Me(NH_2)(SO_3H)_2$ by diazo- reaction (Limpricht, *B.* 18, 2179; E. Richter, *A.* 230, 324).—BaA'' 6aq.—K_2A'' aq.

Chloride $C_6H_2MeBr(SO_2Cl)_2$. [129°-133°].

Amide $C_6H_2MeBr(SO_2NH_2)_2$. [above 240°].

Di-bromo-toluene sulphonic acid $C_6H_2MeBr_2(SO_3H)$. From *o*-bromo-toluene *m*-sulphonic acid by nitration, and displacement of NO_2 by Br (Schäfer, *A.* 174, 365).—NaA' 2aq.—BaA'_2 $2\frac{1}{2}$aq.

Tri-bromo-toluene sulphonic acid $C_6HMeBr_3(SO_3H)$. From *o*-toluidine *p*-sulphonic acid by bromination and exchange of NH_2 for Br (Hayduck, *A.* 174, 351).—KA'.—BaA'_2 $1\frac{1}{2}$aq. The *chloride* is a syrup, the *amide* an amorphous powder.

BROMO-(a)-TOLUIC ACID *v.* Bromo-phenyl-acetic acid.

***p*-Bromo-*o*-toluic acid** $C_6H_3MeBr(CO_2H)$ [1:4:2]. [118° uncor.]. Fine white needles. Formed by oxidation of bromo-*o*-ethyl-toluene with dilute HNO_3 (1·1) at 200° (Claus a. Pieszczek, *B.* 19, 3088).

Bromo-toluic acid $C_6H_3MeBr.CO_2H$ [1:3or4:2]. [167°]. From *o*-toluic acid and bromine in the cold (Jacobsen a. Wierss, *B*, 16, 1959; Racine, *A.* 239, 74). Needles; volatile with steam. On oxidation it gives bromo-phthalic acid [157°].

Salt.—BaA'_2 5aq.

Methyl ether MeA'. [46°].

Bromo-*o*-toluic acid $C_6H_3MeBrCO_2H$ [1:4or5:2]. [176°]. Glistening needles. V. sl. sol. hot water. Formed by oxidation of bromo-*o*-xylene with dilute HNO_3.—CaA'_2 2aq (Jacobsen, *B.* 17, 2375). This acid is perhaps identical with the following.

Bromo-*o*-toluic acid $C_6H_3MeBr(CO_2H)$ [1:5:2]. [187°]. Formed by saponification of the nitrile. Sublimes in needles. V. sol. alcohol, v. sl. sol. water. By alkaline $KMnO_4$ it is oxidised to bromo-phthalic acid [168°] (Nourrisson, *B.* 20, 1016).

Amide $C_6H_3MeBr(CONH_2)$: [182°]; pearly plates (from alcohol); sublimes in needles.

Nitrile $C_6H_3MeBr(CN)$ [1:5:2]. [70°]. Formed from bromo-*o*-toluidine by diazotisation and treatment with cuprous cyanide. Long needles. Easily volatile with steam.

Bromo-*m*-toluic acid $C_6H_3MeBr(CO_2H)$ [1:4:3]. [153°].

Formation.—1. From bromo-isocymene, $C_6H_3MePrBr$ [1:3:4] by treatment with dilute HNO_3 (Kelbe a. Czarnomski, *A.* 235, 296).—2. Together with the following acid, by brominating *m*-toluic acid in the cold (Jacobsen, *B.* 14, 2351).—3. From bromo-nitro-toluene [45°] by treatment with KCN and alcohol at 220°, and saponification of the resulting nitrile (Richter, *B.* 5, 425).

Properties.—Slender needles; sl. sol. cold HOAc. Oxidation gives (4, 1, 3)-bromo-isophthalic acid.

Bromo-*m*-toluic acid $C_6H_3MeBrCO_2H$ [1:6:3]. [209° cor.].

Formation.—1. By oxidation of bromo-*m*-xylene (Fittig, *A.* 147, 32; Jacobsen, *B.* 14, 2352).—2. Together with the preceding by brominating *m*-toluic acid (J.).—3. By oxidising the corresponding bromo-*m*-isocymene (Kelbe, *B.* 15, 41).—4. From the corresponding amido-toluic acid by exchange of NH_2 for Br (Remsen a. Kuhara, *Am.* 3, 431).

Properties.—Crystalline powder, sol. hot alcohol, insol. water.—CaA'_2 3aq.—BaA'_2 4aq.—AgA'.

Ethyl ether EtA'. [c. −5°]; (270°-275°).

Bromo-*p*-toluic acid $C_6H_3MeBr(CO_2H)$ [1:2:4]. [204°].

Formation.—1. By the oxidation of bromo-cymene $C_6H_3MePrBr$ [1:4:2] (Landolph, *B.* 5, 268), bromo-*p*-xylene (Jannasch a. Dieckmann, *A.* 171, 83), bromo-*p*-ethyl-toluene (Remsen a. Morse, *Am.* 1, 138).—2. By brominating *p*-toluic acid in the cold (Brückner, *B.* 9, 407).

Properties.—Thin needles or laminæ (from water); m. sol. hot water.

Salts.—$BaA'_2$4aq.—$CaA'_2$3½aq.—$CaA'_2$3aq.

Bromo-*p*-toluic acid $C_6H_3MeBr(CO_2H)$ [1:3:4]. [196°]. Formed by oxidising bromo-*p*-cymene $C_6H_3MePrBr$ [1:4:3] (Kelbe a. Koschnitzky, *B.* 19, 1731).

Di-bromo-*m*-toluic acid $C_6H_2MeBr_2(CO_2H)$. [186°]. Formed by oxidising crude di-bromo-xylene with CrO_3 (Fittig, Ahrens, a. Mattheides, *A.* 147, 36). Minute needles (from alcohol).—BaA'_2 9aq.—AgA'.

Di-bromo-*p*-toluic acid $C_6H_2MeBr_2.CO_2H$ [4:6:3:1]. [195°]. Needles (from alcohol). V. sl. sol. hot water. Formed by oxidation of di-bromo-*p*-xylene $C_6H_2(CH_3)_2Br_2$ [1:4:3:6] in acetic acid solution with CrO_3. By further oxidation with $KMnO_4$ it gives di-bromo-terephthalic acid $C_6H_2Br_2(CO_2H)_2$ [6:3:4:1].

Salts.—$CaA'_2$4aq: S. 1 at 20°.—BaA'_2 2aq.

Ethyl ether A'Et: [49°]; (c. 310°); long needles (Schultz, *B.* 18, 1762).

BROMO-*o*-TOLUIDINE $C_6H_3Me(NH_2)Br$ [1:2:3]. Formed by reducing bromo-nitro-toluene, itself got by the diazo-reaction from bromo-nitro-toluidine [88°]. Oil. Gives with bromine-water di-bromo-*o*-toluidine, $C_6H_2(CH_3)(NH_2)Br_2$, [47°]. Heated with conc. HCl at 160° it forms the above di-bromo-toluidine and a crystalline bromo-toluidine [55°] (Nevile a. Winther, *C. J.* 37, 630).

Bromo-toluidine $C_6H_3Me(NH_2)Br$ [1:2:4]. [32°]. (c. 255°). Formed by reducing the corresponding bromo-nitro-toluene, [45°] (Hübner a. Wallach, *A.* 154, 298; Körner, *Z.* 1869, 636; Hübner a. Roos, *B.* 6, 799; Wroblewsky, *A.* 168, 177; Heynemann, *Z.* [2] 6, 402; *A.* 158, 340; Nevile a. Winther, *C. J.* 37, 442). Laminæ.—B'HCl: six-sided trimetric tables, S. ·827 at 11·5°.—$B'_2H_2SO_4$.

Bromo-*o*-toluidine $C_6H_3Me(NH_2)Br$ [1:2:5]. [58°]. Formed by brominating acetyl-*o*-toluidine (Wroblewsky, *A.* 168, 162; *Z.* [2] 7, 135). Also from bromo-nitro-toluene [55°] by tin and HCl (Grete, *B.* 8, 565; *A.* 177, 249). Rhombohedra (from alcohol). Its constitution is known because it gives the same di-bromo-toluene (*q. v.*) as bromo-*m*-toluidine. By displacement of NH_2 by H it yields *m*-bromo-toluene.—$B'_2H_2SO_4$.—$B'_2H_2SO_4$ 1½aq.—B'HCl.—$B'HNO_3$: [183°]; S. 4·92 at 17°.

Acetyl derivative $C_6H_3Me(NHAc)Br$. [157°].

Bromo-toluidine $C_6H_3Me(NH_2)Br$ [1:3:4]. [32°] (N. a. W.); [67°] (Wr.); [75°] (H. a. R.). By reducing the corresponding bromo-nitro-toluene (*q. v.*) (Nevile a. Winther, *C. J.* 37, 442; Wroblewsky, *A.* 168, 177; Hübner a. Roos, *B.* 6, 800).

Acetyl derivative $C_6H_3Me(NHAc)Br$. [114°] (N. a. W.).

Bromo-toluidine $C_6H_3Me(NH_2)Br$ [1:3:5]. [36°]. (c. 258°). S.G. 1·1412. Formed by reducing bromo-nitro-toluene, [81°]. Crystallises with difficulty (N. a. W.; Wroblewsky, *A.* 192, 203). Reduced by sodium-amalgam to *m*-toluidine.—B'HCl.—$B'HNO_3$. S. 2·5 at 13°.—$B'_2H_2SO_4$.

Acetyl derivative $C_6H_3Me(NHAc)Br$. [168°].

Bromo-*m*-toluidine $C_6H_3Me(NH_2)Br$ [1:3:6] [78°]. (240°). Formed by brominating acetyl-*m*-toluidine and boiling the product with alcoholic potash (N. a. W.). Formed also by reducing (1,2,5)-$C_6H_3(CH_3)Br(NO_2)$. It gives the same di-bromo-toluene (*q. v.*) as bromo-*o*-toluidine.—$B'HNO_3$: prisms.

Bromo-toluidine $C_6H_3Me(NH_2)Br$. From *o*-bromo-toluene by nitration and reduction (Hübner a. Roos, *B.* 6, 801). Oil.—*B'HCl: S. 3·1 at 16·5°.—*$B'HNO_3$: 1·25 at 19°. Perhaps identical with the preceding.

Bromo-*p*-toluidine $C_6H_3Me(NH_2)Br$ [1:4:3]. [26°] (Claus a. Steinberg, *B.* 16, 914). (240°). S.G. ^{20} 1·50. From acetyl-*p*-toluidine by bromination and saponification (Wroblewsky, *A.* 168, 153). Elimination of NH_2 gives *m*-bromo-toluene.—$B'HNO_3$: [182°]; S. 2·533 at 19°.—$B'H_2SO_4$ aq.—$B'H_2C_2O_4$.

Acetyl derivative $C_6H_3Me(NHAc)Br$. [117·5°].

Bromo-*p*-toluidine $C_6H_3Me(NH_2)Br$ [1:4:2]. [26°]. Formed by reducing the corresponding bromo-nitro-toluene (Nevile a. Winther, *C. J.* 39, 85).—B'HBr.—B'HCl (Wallach, *A.* 235, 255).

Di-bromo-*o*-toluidine $C_6H_2(CH_3)(NH_2)Br_2$ [1:2or6:3:5]. [46°] (N. a. W.); [50°] (Wroblewsky, *A.* 168, 187; *Z.* [2] 7, 210). From *o*-toluidine and bromine (Nevile a. Winther, *C. J.* 37, 436). Forms unstable compounds with strong acids.

Di-bromo-toluidine $C_6H_2(CH_3)(NH_2)Br_2$ [1:x:3:4]. [98°] (N. a. W.); [85°] (Wr.). By reducing the corresponding nitro- compound (Nevile a. Winther, *C. J.* 37, 439; Wroblewsky, *A.* 168, 184). Does not combine with acids.

Di-bromo-*m*-toluidine $C_6H_2Me(NH_2)Br_2$ [1:5:3:4]. [59°]. Formed by reducing the corre-

sponding di-bromo-nitro-toluene (Nevile a. Winther, *C. J.* 37, 447).

Acetyl derivative $C_6H_2(CH_3)(NHAc)Br_2$. [163°].

Di-bromo-*m*-toluidine $C_6H_2Me(NH_2)Br_2$ [1:3:2:5]. [73°]. From the corresponding di-bromo-nitro-toluene [70°] by reduction. V. sol. alcohol (Nevile a. Winther, *C. J.* 37, 448).

Acetyl derivative $C_6H_2(CH_3)(NHAc)Br_2$. [145°].

Di-bromo-*m*-toluidine $C_6H_2Me(NH_2)Br_2$ [1:3:4:6]. [75°]. *Formation.*—1. Acetyl-*m*-toluidine is brominated. The product is boiled with alcoholic KOH and then distilled with dilute acid. This retains bromo-toluidine. By fractionally distilling the rest with steam, two di-bromo-*m*-toluidines [75°] and [35°], and one tri-bromo-toluidine [101°] may be isolated (Nevile a. Winther, *C. J.* 37, 440).—2. By brominating the acetyl derivative of bromo-toluidine [32°], and removing acetyl by heating with H_2SO_4 (2 vols.) and water (1 vol.).

Acetyl derivative $C_6H_2(CH_3)(NHAc)Br_2$. [168°].

Di-bromo-*m*-toluidine $C_6H_2Me(NH_2)Br_2$ [1:3:2:6]. [35°]. Prepared as above.

Di-bromo-*m*-toluidine $C_6H_2Me(NH_2)Br_2$ [1:3:5:6]. [86°]. Prepared by reducing di-bromo-nitro-toluene [105°] (Nevile a. Winther, *C. J.* 37, 434). Formed also by heating the acetyl derivative with equal volumes of H_2SO_4 and water.—B'HCl.

Acetyl derivative $C_6H_2(CH_3)(NHAc)Br_2$. [205°]. Formed by acetylation of the base; also from Br and bromo-acetyl-toluidine [168°].

Di-bromo-*p*-toluidine $C_6H_2Me(NH_2)Br_2$ [1:4:3:5]. [73°] (N. a. W.); [76°] (Wroblewsky). From *p*-toluidine and bromine (Wroblewsky, *A.* 168, 188; Nevile a. Winther, *C. J.* 37, 436). From *p*-toluidine *m*-sulphonic acid and Br (Pechmann, *A.* 173, 216). Converted by N_2O_3 into di-bromo-toluene [39°].

Di-bromo-*p*-toluidine $C_6H_2Me(NH_2)Br_2$ [1:4:2:5]. [85°]. Formed by reducing the corresponding nitro- compound [87°] (Nevile a. Winther, *C. J.* 37, 415; Wroblewsky, *A.* 168, 185). Yields tri-bromo-toluene [111°].

Di-bromo-*p*-toluidine $C_6H_2Me(NH_2)Br_2$ [1:4:2:6]. [88°]. Formed by reduction of the corresponding nitro- compound [57°].

Di-bromo-toluidine $C_6H_2Me(NH_2)Br_2$ [1:4or6:2:3]. [53°]. From the corresponding di-bromo-nitro-toluene [57°] (N. a. W.).

Tri-bromo-*o*-toluidine $C_6HMe(NH_2)Br_3$. [106°]. Described by Gerver (*A.* 169, 379) as formed by brominating *o*-toluidine. Nevile a. Winther (*C. J.* 37, 438) say that no such body is so formed.

Tri-bromo-*m*-toluidine $C_6HMe(NH_2)Br_3$ [1:3:2:5:6]. [94°]. From the acetyl derivative by boiling with alcoholic potash.

Acetyl derivative $C_6H(CH_3)(NHAc)Br_3$. [181°]. From $C_6H_2(CH_3)(NHAc)Br_2$ [1:3:2:5] [144°] and Br (Nevile a. Winther, *C. J.* 37, 448).

Tri-bromo-*m*-toluidine $C_6HMe(NH_2)Br_3$ [1:5:2:3:4]. [96°]. From its acetyl derivative by alcoholic KOH (N. a. W.).

Acetyl derivative $C_6H(CH_3)(NHAc)Br_3$ [1:5:3:4:2]. [173°]. Formed by brominating $C_6H_2(CH_3)(NHAc)Br_2$.

Tri-bromo-*m*-toluidine $C_6HMe(NH_2)Br_3$ [1:5:2:4:6]. [101°] (N. a. W.); [97°] (Wr.). Formed by brominating di-bromo-*m*-toluidine (Nevile a. Winther, *C. J.* 37, 448; Wroblewsky, *A.* 168, 195).

Tri-bromo-*p*-toluidine $C_6HMe(NH_2)Br_3$ [1:4:2:3:5]. [83°]. From the hydro-chloride of $C_6H_3(CH_3)Br(NH_2)$ [1:2:4] and bromine-water (N. a. W.). Needles (from alcohol).

Tri-bromo-*p*-toluidine $C_6HMe(NH_2)Br_3$ [1:4:5:6:2]. [118°]. Formed by reducing the corresponding nitro- compound [106°] by iron and acetic acid (Nevile a. Winther, *C. J.* 39, 85).

Tri-bromo-toluidine $C_6HMe(NH_2)Br_3$. [113°]. From *p*-toluidine *m*-sulphonic acid and Br (Pechmann, *A.* 173, 217).

Tri-bromo-toluidine $C_6HMe(NH_2)Br_3$. [82°]. From *o*-bromo-toluene *m*-sulphonic acid by nitration, reduction and bromination (Schäfer, *A.* 174, 362; *B.* 7, 1355).

Tri-bromo-toluidine $C_6HMe(NH_2)Br_3$. [72°]. From *p*-bromo-toluene *o*-sulphonic acid by similar treatment (S.).

Tetra-bromo-*m*-toluidine $C_6Me(NH_2)Br_4$ [1:3:2:4:5:6]. [224°]. From bromo-*m*-toluidine, [37°], aqueous HCl, and bromine (Nevile a. Winther, *C. J.* 37, 449). White needles (from alcohol).

Tetra-bromo-*p*-toluidine $C_6Me(NH_2)Br_4$ [1:4:2:3:5:6]. [227°]. From $C_6H_2Me(NH_2)Br_2$ [1:4:2:6] dissolved in dilute HCl and treated with bromine-water (Nevile a. Winther, *C. J.* 39, 85). Also from *p*-nitro-toluene, $FeBr_2$, and Br at 90° (Scheufelen, *A.* 231, 179).

BROMO-TOLUIDINE SULPHONIC ACID *v.* BROMO-AMIDO-TOLUENE SULPHONIC ACID.

DI-BROMO-TOLUQUINONE $C_6HMeBr_2O_2$ [85°]. Formed together with the tri-bromo-derivative by the action of bromine on tolu-quinone, and separated from it by crystallisation from dilute acetic acid in which it is the more soluble. Yellow needles; m. sol. water and alcohol (Canzoneri a. G. Spica, *G.* 12, 472).

Tri-bromo-toluquinone $C_6MeBr_3O_2$ [1:3:4:6:2:5]. [235°].

Formation.—1. From toluquinone and Br.—2. From tri-bromo-hydrotoluquinone and Fe_2Cl_6. 3. In small quantities, by heating cresol with H_2SO_4, MnO_2, and KBr (C. a. S.).

Properties.—Pale yellow laminæ; insol. water, sl. sol. alcohol. Aniline forms black crystalline $C_6MeBr(NPhH)_2O_2$. Aqueous KOH forms $C_6MeBr_2(OH)O_2$ [197°] (Spica a. Magnanimi, *G.* 13, 312).

BROMO-*op*-DITOLYL [4:3or2:1] $C_6H_3MeBr.C_6H_4Me$ [1:2]. [95° cor.]. From di-tolyl and Br (Carnelley a. Thomson, *C. J.* 47, 590). Purified by crystallisation from alcohol, from which an oily isomeride first separates. Oxidation gives bromo-terephthalic acid [309° cor.].

Bromo-*op*-ditolyl [4:1] $C_6H_4Me.C_6H_3MeBr$ [1:2:3or6]. Oil; prepared as above. Oxidation gives bromo-diphenic acid [208°] and *c*-bromo-phthalic acid [197°].

Di-bromo-ditolyl $C_{14}H_{12}Br_2$ [152°]. From Br and ditolyl in CS_2 (Carnelley a. Thomson, *C. J.* 47, 591). Long hair-like needles; less soluble in alcohol than the preceding compound. CrO_3 in HOAc gives $C_{14}H_8Br_2O_2$ [166°] and $C_{14}H_8Br_2O_4$ (?) [198°], neither of which compounds dissolves in KOHAq.

BROMO - TOLYL - AMIDO - CHLORO - NAPHTHOQUINONE v. CHLORO-NAPHTHOQUINONE-BROMO-TOLUIDE.

DI - BROMO - *o* - TOLYL - AMIDO - PROPIONITRILE $C_6H_2MeBr_2.CHMe.CN$. [105°]. From *o*-tolyl-amido-propionitrile and Br (Stephan, *C. C.* 1886, 470).

Di-bromo-*p*-tolyl-amido-propionitrile $C_6H_2MeBr_2.CHMe.CN$. [117°]. (S.).

TETRA-BROMO-DI-TOLYL-AMINE $(C_6H_2MeBr_2)_2NH$. [162°]. From Br and di-tolyl-nitrosamine in alcohol (Lehne, *B.* 13, 1544). Small needles.

BROMO-*p*-TOLYL-BENZENE $C_{13}H_{11}Br$ *i.e.* [4:1] $C_6H_4Br.C_6H_4Me$ [1:4]. *Bromo-phenyl-toluene.* [c. 30°]. A product of the bromination of *p*-tolyl-benzene. Oxidation gives bromo-diphenyl-carboxylic acid [194°] and *p*-bromo-benzoic acid (Carnelley a. Thomson, *C. J.* 51, 88).

Bromo-*p*-tolyl-benzene $C_6H_5.C_6H_3MeBr$ [1:2or3:4]. [129°]. From tolyl-benzene in CS_2 by Br (Carnelley a. Thomson, *C. J.* 47, 586; 51, 87). Pearly plates, sl. sol. hot alcohol, v. e. sol. benzene. Oxidises to bromo-terephthalic acid [306° cor.].

Di-bromo-*p*-tolyl-benzene [4:1] $C_6H_4Br.C_6H_3BrMe$ [1:2or3:4]. [115°]. From *p*-tolyl-benzene in CS_2 and Br (Carnelley a. Thomson, *C. J.* 51, 89). Oxidation gives di-bromo-diphenyl-carboxylic acid [204°] and *p*-bromo-benzoic acid.

Di-bromo-tolyl-benzene [4:1] $C_6H_4Br.C_6H_3BrMe$ [1:3or2:4]. [150°]. Formed, together with the isomeride [115°] in brominating *p*-tolyl-benzene. Oxidation gives di-bromo-diphenyl-carboxylic acid [232°] and *p*-bromo-benzoic acid.

BROMO-TOLYLENE-*m*-DIAMINE $C_6H_2(CH_3)(NH_2)_2(Br)$ [1:2:4:*x*]. [104°]. Colourless plates. Sol. alcohol, ether, and CS_2. Prepared by bromination of the di-benzoyl-derivative of (1:2:4)-tolylene-diamine and subsequent saponification.

Di-benzoyl-derivative [214°]. White needles (Ruhemann, *B.* 14, 2658).

Bromo-tolylene diamine $C_6H_2(CH_3)(NH_2)_2Br$. [107°]. Formed by reducing bromo-di-nitro-toluene [104°] (Grete, *A.* 177, 262).—$B''2HCl$.—$B''2HNO_3$.—$B''H_2SO_4$.—$B''H_2C_2O_4$. This body is perhaps identical with the preceding.

Bromo-tolylene-*o*-diamine $C_6H_2(CH_3)(NH_2)_2Br$ [1:2:3:4]. [59°]. Obtained by nitration and reduction of *p*-bromo-*o*-toluidine (Hübner a. Schüpphaus, *B.* 17, 775). Small colourless needles. V. sol. water, alcohol, and benzene.

Salts.—$B'HCl$: very soluble colourless needles.—$B'_2H_2SO_4$: colourless tables.

Anhydro-formyl derivative v. METHENYL-BROMO-TOLYLENE-*o*-DIAMINE.

BROMO-TOLYL-ETHANE v. BROMO-ETHYL-TOLUENE.

α-BROMO-α-*m*-TOLYL-ETHYLENE $C_7H_7.CBr:CH_2$. Formed by boiling *m*-tolyl di-bromo-ethane $C_7H_7.CHBr.CH_2Br$ with alcoholic KOH. Very unstable body: begins to blacken even at 100° (Müller, *B.* 20, 1216).

ω-Bromo-α-*m*-tolyl-ethylene $C_7H_7.CH:CHBr$. *m-Methyl-bromo-styrene.* (242°). Oil. Formed by adding bromine to a warm solution of sodium *m*-tolyl-acrylate (methyl-cinnamate) (Müller, *B.* 20, 1216).

BROMO-TOLYL MERCAPTAN $C_6H_3MeBr.SH$. [c. 7°]. (c.245°). From *p*-bromo-toluene sulphochloride, tin, and HCl (Hübner a. Wallach, *Z.* [2] 5, 500).

Bromo-tolyl mercaptan $C_6H_3MeBr.SH$. (246°). From *o*-bromo-toluene *m*-sulphochloride [53°] by Zn and H_2SO_4 (Hübner, *A.* 169, 41). Oil.

DI-BROMO-DI-TOLYL-METHANE $C_{15}H_{14}Br_2$. [115°]. From the hydrocarbon and Br (Weiler, *B.* 7, 1181).

BROMO-*p*-TOLYL-*p*-METHYL-IMESATIN v. *p*-METHYL-ISATIN-BROMO-*p*-TOLUIDE.

TETRA-BROMO-*p*-TOLYL-(β)-NAPHTHYL-AMINE $C_{17}H_{11}Br_4N$. [169°]. Formed by bromination of *p*-tolyl-(β)-naphthyl-amine (Friedländer, *B.* 16, 2080). White silky needles. Sol. alcohol and ether.

BROMO - DI - α - TOLYL - PROPIONIC ACID $C_6H_4MeBr.C(C_6H_4Me)Me.CO_2H$. [144°]. Colourless crystals. Sol. alcohol, ether, &c. Formed by bromination of di-α-tolyl-propionic acid (Haiss, *B.* 15, 1178).

αβ-DI-BROMO-*m*-TOLYL-PROPIONIC ACID $C_{10}H_{10}Br_2O_2$ *i.e.* [3:1] $C_6H_4Me.CHBr.CHBr.CO_2H$. [167°]. From *m*-methyl-cinnamic acid and Br (Müller, *B.* 20, 1215).

DI - BROMO - DI - TOLYL - DI - SULPHIDE $(C_6H_3MeBr)_2S_2$. [78°]. From *o*-bromo-tolyl mercaptan and dilute HNO_3 (Hübner a. Post, *A.* 169, 42).

BROMO-UMBELLIFERON

Methyl ether $\left[4\ \tfrac{1}{2}\right]$ $C_6H_2(OMe)\langle{}^{CH:CBr}_{O\,.\,CO}\rangle$. [154°]. Formed by the action of bromine upon a solution of umbelliferon-methyl ether in CS_2. Long white needles; m. sol. hot alcohol and ether, sl. sol. cold alcohol and ether, insol. water; its dilute alcoholic solution has a green fluorescence. By alcoholic KOH it is converted into methoxy-coumarilic acid

$C_6H_3(OMe)\langle{}^{CH:C.CO_2H}_{O}\rangle$

Ethyl ether $C_6H_2(OEt)\langle{}^{CH:CBr}_{O\,.\,CO}\rangle$: [116°] silvery tables; sol. boiling alcohol and ether, sl. sol. cold alcohol; its dilute alcoholic solution has a violet fluorescence. Analogous to the methyl-ether in its formation and properties (Will a. Beck, *B.* 19, 1782).

Di-bromo-umbelliferon

$C_6H_2Br(OH)\langle{}^{CH:CBr}_{O-CO}\rangle$ (?).

Methyl ether $C_6H_2Br(OMe)\langle{}^{CH:CBr}_{O-CO}\rangle$: [251°]; formed by bromination of umbelliferon-methyl-ether dissolved in acetic acid; white glistening needles; sl. sol. alcohol.

Ethyl ether $C_6H_2Br(OEt)\langle{}^{CH:CBr}_{O-CO}\rangle$: [216°]; formed by bromination of umbelliferon-ethyl-ether in acetic acid (Will a. Beck, *B.* 19, 1786).

Tri-bromo-umbelliferon $C_9H_3Br_3O_3$. [194°]. From umbelliferon and bromine-water (Posen, *B.* 14, 2746; Mössmer, *A.* 119, 261). The alcoholic solution shows greenish-yellow fluorescence.

BROMO-UVITIC ACID $C_6H_2Br(CH_3)(CO_2H)_2$ [x:1:3:5]. Prepared by oxidising bromo-ω,ω_2-di-oxy-mesitylene with $KMnO_4$ (Colson, *A. Ch.* [6] 6, 102). White crystals, carbonises at 285° without melting. Sol. alcohol.—Na_2A'': tables.

α-BROMO-*n*-VALERIC ACID $C_5H_9BrO_2$ *i.e.* $C_3H_7.CHBr.CO_2H$. Formed by bromination of valeric acid (propyl-acetic acid) (Juslin, *B.* 17, 2504).

Ethyl ether A'Et: (191°); S.G. $\frac{18}{4}$ = 1·226; colourless fluid.

γ-Bromo-*n*-valeric acid $CH_3.CHBr.CH_2.CH_2.CO_2H$. From allyl-acetic acid and conc. HBrAq at 0° (Messerschmidt, *A.* 208, 94). Boiling water or cold Na_2CO_3Aq convert it into the lactone of γ-oxy-valeric acid (*q.v.*).

α-Bromo-isovaleric acid $(CH_3)_2CH.CHBr.CO_2H$ (chiefly). [40°]. (230°). From ordinary valeric acid and Br (Cahours, *A. Suppl.* 2, 74; Borodine, *A.* 119, 121; Fittig a. Clark, *A.* 139, 199; Ley a. Popoff, *A.* 174, 63; Schmidt, *A.* 193, 104). Formed also by the action of water on its bromide which is formed by treating isovaleric acid with Br and P (Volhard, *A.* 242, 163). Oil.

Ethyl ether EtA'. (186°). Is best purified by distillation with steam, the liquid is collected as soon as the oily drops sink under water (Lovén, *J. pr.* [2] 33, 112).

Bromo-valeric acid $CMeEtBr.CO_2H$ or, possibly, $CH_3.CHBr.CHMe.CO_2H$ *Bromo-methyl-ethyl-acetic acid. Bromo-hydro-tiglic acid.* [66°]. From tiglic and angelic acids with conc. HBrAq at 0° (Fittig a. Pagenstecher, *A.* 195, 108, 128; *cf.* p. 267). Monoclinic tables (from CS_2); insol. cold water. Boiling water forms tiglic acid and some pseudo-butylene (*s*-di-methyl-ethylene). Na_2CO_3Aq produces chiefly pseudo-butylene. Sodium-amalgam forms methyl-ethyl-acetic acid.

Bromo-valeric acid $C_5H_9BrO_2$ *i.e.* $CMeEtBr.CO_2H$? From methyl-ethyl-acetic acid and Br at 160° (Böcking, *A.* 204, 23). Liquid. Should be identical with the preceding.

Ethyl ether EtA'. (185°). S.G. $\frac{18}{4}$ 1·2275. Decomposed by boiling Na_2CO_3Aq into α-methyl-α-oxy-butyric ether $CMeEt(OH).CO_2Et$.

$\gamma\delta$-Di-bromo-*n*-valeric acid $CH_2Br.CHBr.CH_2.CH_2.CO_2H$. [58°]. From allyl-acetic acid and Br in CS_2 (Messerschmidt, *A.* 208, 100). Thin laminæ. Converted by sodium-amalgam into allyl-acetic acid. Boiling water forms the lactone of bromo-oxy-valeric acid, and finally $C_5H_8O_3$.

Di-bromo-valeric acid $CMe_2Br.CHBr.CO_2H$. [106°]. Solidifies at 76°. From $CMe_2:CH.CO_2H$ and bromine (Ustinoff, *J. pr.* [2] 34, 483).

Di-bromo-valeric acid $CH_3.CHBr.CBrMe.CO_2H$. [86°]. From tiglic acid and Br (Schmidt a. Berendes, *A.* 191, 119); also from angelic acid and Br (Jaffé, *A.* 135, 293; Pagenstecher, *A.* 195, 123). Triclinic crystals (from CS_2); insol. cold water. Converted by distillation or by sodium-amalgam into tiglic acid (Demarçay, *B.* 8, 830). Boiling water decomposes its salts forming bromo-butinene (87°).—KA': insol. conc. KOHAq.

Ethyl ether EtA'. (185°). (J.).

DI-BROMO-VALERIC ALDEHYDE $C_5H_8Br_2O$ *i.e.* $CH_3.CHBr.CBrMe.CHO$. From tiglic aldehyde and Br (Lieben a. Zeisel, *M.* 7, 55).

BROMO-VALERO-LACTONE *v.* BROMO-OXY-VALERIC ACID.

BROMO-VALERYLENE C_5H_7Br. (125°–130°). From valerylene dibromide and alcoholic KOH (Reboul, *A.* 135, 372). Forms a yellow pp. of C_5H_5Cu with ammoniacal cuprous chloride.

BROMO-VANILLIC ACID *v. Methyl derivative* of BROMO-DI-OXY-BENZOIC ACID.

BROMO-VERATRIC ACID *v. Methyl derivative* of BROMO-DI-OXY-BENZOIC ACID.

BROMO-VINYL ACETATE $C_4H_5BrO_2$ *i.e.* $CHBr:CH.OAc$. From acetylene di-bromide and KOAc at 160° for 2 days (Sabanejeff, *A.* 216, 272). Crystals. Explode when quickly heated. Forms with bromine a compound $C_4H_4Br_2O_2$, which solidifies at 0°.

ω-BROMO-*p*-VINYL-PHENOL. *Methyl ether* $C_6H_4(OMe).CH:CHBr$. [55°]. From the di-methyl-ether of $\alpha\beta$-di-bromo-*p*-oxy-phenyl-propionic acid $C_6H_4(OMe).CHBr.CHBr.CO_2Me$ by boiling with aqueous KOH (30 p.c.). Plates, of pleasant smell and taste (Eigel, *B.* 20, 2537).

***eso*-Bromo-*o*-vinyl-phenol** $C_6H_3(OH)Br.CH:CH_2$. *Bromo-oxy-styrene.* (265°). Formed by distilling di-bromo-ethyl-phenol, $C_6H_3(OH)Br.C_2H_4Br$ obtained by brominating *o*-ethyl-phenol (Suida a. Plohn, *M.* 1, 180). Liquid, sl. sol. water. Gives a reddish-brown pp. with Fe_2Cl_6.

Di-bromo-*o*-vinyl-phenol. *Methyl ether* $C_9H_8Br_2O$ *i.e.* $C_6H_3(OMe)Br.C_2H_2Br$. From the methyl derivative of tri-bromo-oxy-phenyl-propionic acid $C_6H_3(OMe)Br.CHBr.CHBr.CO_2H$ and Na_2CO_3Aq (Perkin, *C. J.* 39, 418). Oil; slightly volatile with steam.

BROMO-VINYL-PIPERIDINE $C_5H_{10}N(C_2H_2Br)$. *Piper-ethyl-alkine-bromide.* Formed by heating the hydrobromide of piper-ethyl-alkine (oxethyl-piperidine) with 1 mol. of bromine at 100°-120°. On reduction with sodium-amalgam it yields ethyl-piperidine.—B'HBr: thin colourless prisms, sol. water, v. sl. sol. cold alcohol.—B'HCl. — $B'_2H_2Cl_2PtCl_4$.—$B'HCl,AuCl_3$. (Ladenburg, *B.* 17, 154).

BROMO-*o*-XYLENE C_8H_9Br *i.e.* $C_6H_3(CH_3)_2Br$ [1:2:4]. [0°]. (214° i.V.). Mol. w. 185°. S.G. $\frac{15}{15}$ 1·37. Formed by the action of bromine in presence of iodine upon *o*-xylene in the cold and in the dark (Jacobsen, *B.* 17, 2372; Schramm, *B.* 18, 1278).

ω-Bromo-*o*-xylene $C_6H_4(CH_3).CH_2Br$. *o-xylyl bromide.* [21°]. (217°) at 742 mm. S.G. $\frac{23}{}$ 1·381. Colourless liquid. Prepared by the action of bromine-vapour upon boiling *o*-xylene; or in the cold upon *o*-xylene exposed to direct sunshine (Radziszewski a. Wispek, *B.* 15, 1747; 18, 1281; Schramm, *B.* 18 1278; Colson, *A. Ch.* [6] 6, 115).

Bromo-*m*-xylene $C_6H_3(CH_3)_2Br$ [1:3:4]. (206°). Formed by the action of bromine upon cold *m*-xylene in the dark (Fittig, *A.* 147, 31; Schramm, *B.* 18, 1277). MeI and Na give ψ-cumene.

(β)-Bromo-m-xylene $C_6H_3Me_2Br$ [1:3:2]. (c. 206°). Liquid at −10°. Obtained by adding a HCl solution of bromine to a solution of sodium *m*-xylene-(β)-sulphonate, which is prepared by debrominating di-bromo-*m*-xylene sulphonic acid $C_6HMe_2Br_2(SO_3H)$ [1:3:4:6:2] with zinc-dust and aqueous ammonia. By methyl iodide and sodium it gives hemimellithene $C_6H_3Me_3$ [1:2:3] (Jacobsen a. Deike, *B.* 20, 903).

Bromo-xylene $C_6H_3Me_2Br$ [1:3:5]. (204°). S.G. $\frac{22}{}$ 1·362. Oil. From $C_6H_3Me_2(NH_2)$ [1:3:4] *viâ* $C_6H_3Me_2HHAc$, $C_6H_2BrMe_2NHAc$ and $C_6H_2BrMe_2(NH_2)$ (Wroblewsky, *A.* 192, 215; *B.* 9, 495).

ω-Bromo-m-xylene $C_6H_4(CH_3).CH_2Br$. *m-Xylyl bromide.* (215°) at 735 mm. (R. a. W.); (c. 218°) (C.). S.G. $\frac{23}{}$ 1·371. Colourless liquid, with pungent vapour. Prepared by the action of the vapour of bromine on boiling *m*-xylene, or from Br (1 mol.) and cold *m*-xylene exposed to direct sunlight (Radziszewski a. Wispek, *B.* 15, 1745; 18, 1282; Schramm, *B.* 18, 1277; Colson, *A. Ch.* [6] 6, 117).

Bromo-p-xylene $C_6H_3Br(CH_3)_2$ [2:1:4]. [10°]. (206° i.V.). Formed by the action of bromine upon cold *p*-xylene in the dark (Fittig a. Jannasch, *A.* 151, 283; 171, 82; *B.* 17, 2709; Jacobsen, *B.* 18, 356; Schramm, *B.* 18, 1276). Large plates.

ω-Bromo-p-xylene $C_6H_4(CH_3).CH_2Br$. *p-Xylyl bromide.* [36°]. (219°) at 740 mm. Long colourless needles. Sol. ether and chloroform. Pungent smell. Prepared by the action of bromine-vapour on boiling *p*-xylene, or of Br (1 mol.) upon cold *p*-xylene exposed to direct sunshine (Radziszewski a. Wispek, *B.* 15, 1743; *B.* 18, 1279; Schramm, *B.* 18, 1277).

Di-bromo-o-xylene $C_6H_2(CH_3)_2Br_2$ [1:2:3:4?]. [7°]. (277°). S.G. $\frac{15}{15}$ 1·7812. Liquid at ordinary temperatures. Formed together with the isomeride [88°] by the action of bromine (2 mols.) in presence of iodine upon *o*-xylene (1 mol.) in the cold (Jacobsen, *B.* 17, 2376).

Di-bromo-o-xylene $C_6H_2(CH_3)_2Br_2$ [1:2:4:5]. [88°]. (278°). Large trimetric plates, or long needles. V. sol. hot alcohol; v. sl. sol. alcohol at 0°. Formed as above (Jacobsen, *B.* 17, 2376).

o-Di-ω-bromo-xylene $C_6H_4(CH_2Br)_2$ [1:2]. *o-Xylylene bromide.* [95°]. S.G. $\frac{0}{}$ 1·934. S. (ether) 20. S.H. (15°–40°) ·183. Splendid large trimetric crystals. Prepared by heating *o*-xylene with bromine (2 mols.) at 130°–155°. Also by the action of Br (2 mols.) in the cold upon *o*-xylene (1 mol.) exposed to direct sunshine. Trimetric crystals; $a:b:c = \cdot 8581:1:\cdot 5014$; v. sol. ether and chloroform. By boiling with a solution of Na_2CO_3 for 3 hours it yields phthalyl-alcohol (Baeyer a. Perkin, *B.* 17, 123; Radziszewski a. Wispek, *B.* 18, 1281; Schramm, *B.* 18, 1278; Colson, *A. Ch.* [6] 6, 105; *C. R.* 101, 428; Perkin, jun., *C. J.* 53, 5).

Di-bromo-m-xylene $C_6H_2(CH_3)_2Br_2$. [72°]. (256°). From *m*-xylene and Br (Fittig, *A.* 147, 25; 156, 236).

Di-bromo-m-xylene $C_6H_2(CH_3)_2Br_2$. (252°). Liquid. From brominated *m*-xylidine by the diazo- reaction (Wroblewsky, *A.* 192, 216).

ω₁ω₂-Di-bromo-m-xylene $C_6H_4(CH_2Br)_2$ [1:3]. *Xylylene dibromide.* [77°]. S.G. $\frac{2}{}$ 1·734; $\frac{22}{}$ (liquid) 1·615. S. (ligroïn) 33. S.H. (15°–40°) ·184. Formed by the action of bromine (2 mols.) in the cold upon *m*-xylene exposed to direct sunshine; also by adding Br (2 mols.) to *m*-xylene at 130°–180° (Schramm, *B.* 18, 1277; Radziszewski a. Wispek, *B.* 18, 1282; Colson, *A. Ch.* [6] 6, 109, *C. R.* 101, 428; Kipping, *C. J.* 53, 26). Prismatic needles (from $CHCl_3$). Attacks the eyes. Converted by alcohol or boiling water into $C_6H_4(CH_2OH)_2$. Alkaline permanganate forms isophthalic acid.

Di-bromo-p-xylene $C_6H_2(CH_3)_2Br_2$ [1:4:2:5]. [76°]. (261°). From *p*-xylene, Br, and I. A small quantity of a liquid isomeride, $C_6H_2(CH_3)_2Br_2$ [1:4:2:6] (?) is formed at the same time. Large triclinic crystals, plates, or flat needles (Jacobsen, *B.* 18, 358; Fittig, Ahrens a. Mattheides, *A.* 147, 26; Jannasch, *B.* 10, 1357).

ω₁ω₂-Di-bromo-p-xylene $C_6H_4(CH_2Br)_2$ [1:4]. *p-Xylylene bromide.* [144°]. (c. 245°). S. (ether) 2·65 at 20°. S.H. (15°–40°) ·180. Formed by the action of bromine (2 mols.) in the cold upon *p*-xylene exposed to direct sunshine; or by the action of bromine-vapour on boiling *p*-xylene (Grimaux, *Z.* 1870, 394; Schramm, *B.* 18, 1277; Radziszewski a. Wispek, *B.* 15, 1744; 18, 1279; Löw, *A.* 231, 362; *B.* 18, 2072; Colson, *C. R.* 101, 428; *A. Ch.* [6] 6, 119; Kipping, *C. J.* 53, 31). Plates; sol. $CHCl_3$. Boiled with water (20 pts.) and lead nitrate (1 pt.) it forms terephthalic aldehyde and some terephthalic acid and *p*-aldehyde-benzoic acid. Fuming HNO_3 acts similarly. Alcohol converts it into $C_6H_4(CH_2OH)_2$; the rate of this saponification is less than with the *o*-, and still less than with the *m*-isomeride.

exo-Tri-bromo-p-xylene $C_6H_4(CHBr_2)(CH_2Br)$. [106°]. Formed from *p*-xylene and impure bromine-vapour (Löw, *A.* 231, 363). Boiling water gives ω-oxy-toluic aldehyde.

Tetra-bromo-o-xylene $C_6(CH_3)_2Br_4$. [262°] (J.); [255°] (B.). (375°). From *o*-xylene and Br (Jacobsen, *B.* 17, 2378) in presence of Al_2Br_6 (Blümlein, *B.* 17, 2492). Long glistening needles. V. sl. sol. hot alcohol; v. sol. hot benzene.

Tetra-bromo-p-xylene $C_6(CH_3)_2Br_4$. [253°]. (355°). From *p*-xylene and Br (Jacobsen, *B.* 18, 359).

BROMO-o-XYLENE-SULPHONIC ACID $C_6H_2(CH_3)_2(Br)(SO_3H)$ [1:2:4:5]. Formed by sulphonation of bromo-*o*-xylene. Crystals (containing aq). Very soluble in water, sparingly in cold dilute H_2SO_4.

Salts.—NaA' $1\frac{1}{2}$aq: long fine needles, v. sol. hot water.—KA' aq.—BaA'_2 3aq: long thick prisms, sol. hot water.

Amide $C_6H_2(CH_3)_2(Br)(SO_2NH_2)$: [213°]; long fine needles, v. sl. sol. water, sl. sol. cold alcohol (Jacobsen, *B.* 17, 2373).

Bromo-o-xylene-sulphonic acid $C_6H_2(CH_3)_2Br(SO_3H)$. Formed by the action of bromine upon an aqueous solution of *o*-xylene-sulphonic acid.—BaA'_2 4aq: sparingly soluble needles.

Amide $C_6H_2Me_2Br.SO_2NH_2$: [187°]; thick needles; v. sol. hot alcohol (Kelbe a. Stein, *B.* 19, 2137).

Bromo-*m*-xylene sulphonic acid $C_6H_2(CH_3)_2Br(SO_3H)$ [1:3:2:4]. From di-bromo-*m*-xylene sulphamide by sodium-amalgam (Jacobsen a. Weinberg, *B.* 11, 1535).

Amide $C_6H_2Me_2BrSO_2NH_2$. [161° cor.].

Bromo-*m*-xylene sulphonic acid $C_6H_2Me_2Br(SO_3H)$ [1:3:6:4]. From $C_6H_3Me_2(SO_3H)$ [1:3:4] by Br or from $C_6H_3Me_2Br$ [1:3:6] by fuming H_2SO_4 (Weinberg, *B.* 11, 1062). From $C_6H_2Me_2(NH_2)(SO_3H)$ by diazo- reaction (Sartig, *A.* 230, 335; Nölting a. Kohn, *B.* 19, 139; Limpricht, *B.* 18, 2180). Slender needles, v. e. sol. water.

Salts.—BaA'_2 aq.—NaA' aq.—ZnA'_2 9aq.—CuA'_2 7aq.

Chloride [61°]: large prisms.

Amide [194°]: small trimetric prisms.

Bromo-*p*-xylene sulphonic acid $C_6H_2Me_2Br.SO_3H$ [1:4:2:5]. Formed by heating diazo-*p*-xylene-sulphonic acid $C_6H_2Me_2<\begin{matrix}N_2\\SO_3\end{matrix}>$ [1:4:2:5] with strong HBr. — BaA'_2 2aq: small white plates.

Chloride: [78°]; small white prisms.

Amide: [201°]; small white plates, v. sol. alcohol and ether, sl. sol. water, benzene, and chloroform (Nölting a. Kohn, *B.* 19, 141).

Bromo-*p*-xylene-sulphonic acid $C_6H_2(CH_3)_2(Br)(SO_3H)$ [1:4:2:*x*]. Pearly plates or flat needles. Formed by sulphonation of bromo-*p*-xylene.

Salts.—NaA' aq: long thin prisms, trimetric plates, or six-sided plates.—BaA'_2: small prisms or thin six-sided plates.

Amide $C_6H_2(CH_3)_2(Br)(SO_2NH_2)$. [206°], flat prisms, v. sol. hot alcohol (Jacobsen, *B.* 17, 2378). This acid is perhaps identical with the preceding.

Di-bromo-*m*-xylene sulphonic acid $C_6H(CH_3)_2Br_2(SO_3H)$ [1:3:4:6:2]. From di-bromo-*m*-xylene [72°] and fuming H_2SO_4 (Jacobsen a. Weinberg, *B.* 11, 1534). Leaflets, sl. sol. cold water. Reduced by sodium-amalgam to (1,3,2)-*m*-xylene sulphonic acid.

Salts.—BaA'_2.—NaA' 2aq: leaflets.

Chloride [107°]: rhombic leaflets.

Amide [220°]: slender needles.

BROMO-*m*-XYLENOL $C_6H_2(CH_3)_2Br(OH)$ [1:3:*x*:4]. From Br and *m*-xylenol in HOAc. Liquid (Jacobsen, *B.* 11, 24).

Bromo-*p*-xylenol $C_6H_2(CH_3)_2Br(OH)$ [1:4:*x*:2]. [87°]. From *p*-xylenol and Br (Jacobsen, *B.* 11, 27).

Di-bromo-*m*-xylenol $C_6H(CH_3)_2Br_2(OH)$ [1:3:?:?:4] [73°] (J.).

$\omega_1\omega_2$ Di-bromo-*p*-xylenol $C_6H_3(CH_2Br)_2(OH)$ [1:4:2]. [74°]. S. (alcohol) 200. From *p*-xylenol and Br at 160° (Adam, *Bl.* [2] 41, 288). Needles; insol. water, but decomposed on boiling with it, HBr coming off.

Tri-bromo-*o*-xylenol $C_6(CH_3)_2Br_3.OH$ [1:2:4:5:6:3]. [184°]. Fine needles. Formed by bromination of *o*-xylenol $C_6H_3(CH_3)_2.OH$ [1:2:3] (Thöl, *B.* 18, 2562).

Tri-bromo-*o*-xylenol $C_6(CH_3)_2Br_3(OH)$ [1:2:3:5:6:4]. [169°]. From (1,2,4)-*o*-xylenol. Felted needles (Jacobsen, *B.* 11, 28).

Tri-bromo-*m*-xylenol $C_6(CH_3)_2Br_3(OH)$ [1:3:2:5:6:4]. [179°]. From (1,3,4)-*m*-xylenol (J.). Long needles.

Tri-bromo-*m*-xylenol $C_6(CH_3)_2Br_3.OH$ [1:3:2:4:6:5]. [166°]. Fine white needles. From *m*-xylenol $C_6H_3(CH_3)_2.OH$ [1:3:5] (Nölting a. Forel, *B.* 18, 2679; *cf.* Thöl, *B.* 18, 362).

Tri-bromo-*p*-xylenol $C_6(CH_3)_2Br_3(OH)$. [175°]. Golden yellow needles (Jacobsen, *B.* 11, 26).

BROMO-*m*-XYLIDINE $C_8H_{10}BrN$ *i.e.* $C_6H_2(CH_3)_2Br(NH_2)$ [1:3:5:4]. [97°]. From acetyl-*m*-xylidine by bromination and saponification. Minute needles (from dilute alcohol). Converted by the diazo-reaction into *s*-bromo-xylene (Genz, *B.* 3, 225; Wroblewsky, *A.* 192, 215).

Di-bromo-*o*-xylidine $C_6H(CH_3)_2Br_2.NH_2$ [1:2:4:5:3]. [103°]. Obtained by reduction of the corresponding nitro-compound with iron and acetic acid. Colourless needles. V. sol. alcohol ether, and acetic acid. Does not form salts. By sodium-amalgam it is debrominated (Thöl, *B.* 18, 2562).

Di-bromo-*m*-xylidine $C_6H(CH_3)_2Br_2(NH_2)$. From acetyl-*m*-xylidine by brominating and saponifying (Genz, *B.* 3, 225). Needles (from alcohol).

Di-bromo-*p*-xylidine $C_6HMe_2Br_2(NH_2)$ [1:4:5:*x*:2]. [65°]. Formed by acidifying an alkaline solution of (1 mol. of) *p*-xylidine-sulphonic acid $C_6H_2Me_2(NH_2)(SO_3H)$ [1:4:2:5] and (2 mols. of) bromine. Also formed by bromination of *p*-xylidine (Nölting a. Kohn, *B.* 19, 142).

BROMO-*m*-XYLIDINE-SULPHONIC ACID $C_6HMe_2(Br)(NH_2)(SO_3H)$ [1:3:5?:4:6]. Small white needles. Sol. hot, v. sl. sol. cold water, insol. alcohol. Formed by bromination of *m*-xylidine-sulphonic acid $C_6H_2Me_2(NH_2)(SO_3H)$ [1:3:4:6] (Nölting a. Kohn, *B.* 19, 140).

Bromo-*p*-xylidine-sulphonic acid $C_6HMe_2Br(NH_2)(SO_3H)$ [1:4:*x*:6:2]. Small white plates. Nearly insoluble in cold water. Formed by bromination of *p*-xylidine-sulphonic acid $C_6H_2Me_2(NH_2)(SO_3H)$ [1:4:6:2].—A'K (Nölting a. Kohn, *B.* 19, 143).

DI-BROMO-*m*-XYLOQUINONE $C_6Br_2Me_2O_2$ [1:3:4:6:2:5]. [174°]. From mesitol, $C_6H_2Me_3(OH)$ and Br in water (Jacobsen, *A.* 195, 271). Golden laminæ (from alcohol), insol. water and Na_2CO_3Aq, decomposed by KOHAq.

Di-bromo-*p*-xyloquinone $C_6Br_2Me_2O_2$ [1:4:5:2:3:6]. [184°]. Formed by the action of bromine upon *p*-xyloquinone under water. Thin golden plates. Insol. water and cold alcohol; sol. ether and benzene (Carstanjen, *J. pr.* [2] 23, 434).

BRONZE *v.* Copper, alloys of.

BRUCINE $C_{23}H_{26}N_2O_4$ 4aq. [105°, hydrated]; [178°, anhydrous] (Claus, *B.* 14, 773); [151°] (Blyth). S. ·12 at 15°; ·2 at 100°. $[\alpha]_D = -85°$ (in alcohol); $-110°$ to $-127°$ (in $CHCl_3$) (Oudemans, *A.* 166, 69).

Occurrence.—Together with strychnine in nux vomica (the seeds of *Strychnos nux vomica*), in the bean of St. Ignatius (the seed of *Strychnos Ignatii*), in the wood of *Strychnos colubrina*, in *upas tiente*, extracted from the bark of *S. tiente*, and in the bark of *Strychnos nux vomica* (*False Angustura bark*) (Pelletier a. Caventou, *A. Ch.* [2] 12, 118; 26, 53; Pelletier a. Dumas, *A. Ch.* [2] 24, 176; Corriol, *J. Ph.* 11, 495; Liebig, *A. Ch.* [2] 47, 172; *A.* 26, 50; Regnault, *A. Ch.* [2] 68, 113). Brucine, free from strychnine,

occurs in the bark of *Strychnos Ligustrina* (*Bidara Laut*) (Greenish, *Ph.* [3] 9, 1013).

Preparation.—Nux vomica seeds (56 lbs.) are powdered and exhausted with alcohol, to which one-sixth part of water has been added. The alcohol is boiled off and the residue treated with water (40 lbs.) containing H_2SO_4 (·12 lbs.). The filtrate is neutralised with Na_2CO_3. The pp. is collected after a few hours, dissolved in chloroform, and the solution shaken with very dilute H_2SO_4 which dissolves brucine. The solution is placed under a bell jar together with a beaker containing ammonia so that neutralisation proceeds very slowly. The crystalline pp. is extracted with dilute alcohol, which dissolves brucine, and the solution allowed to evaporate. The brucine, containing strychnine, is dissolved in dilute H_2SO_4, and the faintly alkaline solution mixed with KI. The brucine hydriodide that is ppd. is crystallised several times from alcohol. It is then shaken with aqueous Na_2CO_3 and chloroform, the chloroform is then shaken with dilute acid and the base pp. with ammonia (W. A. Shenstone, *C. J.* 39, 453).

Properties.—Monoclinic efflorescent prisms (from dilute alcohol); v. sol. alcohol, chloroform, and essential oils, insol. ether and fatty oils. Feebly alkaline to litmus or phenol-phthaleïn (Plugge, *Ar. Ph.* [3] 25, 45). It is lævorotatory, the extent of rotation depending upon the nature of the solvents and the concentration of the solution. In presence of free acids $[\alpha]_D$ varies from $-29°$ to $-36·5°$ (Tykociner, *R. T. C.* 1, 144). Commercial brucine usually contains strychnine, but the colour which strychnine gives with oxidising agents is masked by the presence of brucine. The strychnine may, however, be detected by adding dilute HNO_3 and then extracting the strychnine with chloroform in presence of excess of KOH (Shenstone, *Ph.* [3] 8, 445; Hanriot, *C. R.* 97, 267). Brucine is affected by heating with acids, alkalis, or even water, and hence much is lost by the usual method of preparation, but the products being usually amorphous, the unaltered brucine is easily separated in a pure state.

Colour tests.—*V.* p. 124. The most characteristic is the red colour with nitric acid, which, after warming, is turned violet by excess of ammonium sulphide (*v.* also Cotton, *Z.* [2] 5, 728; *J. Ph.* [4] 10, 18; Luck, *Z.* [2] 6, 275; Le Linde, *C. N.* 37, 98; Flückiger, *Fr.* 15, 312; Hager, *Fr.* 11, 201; Dragendorff, *Fr.* 18, 108; Pandis, *C. C.* 1872, 410; Struve, *Fr.* 12, 164; Buckingham, *Ph.* [3] 3, 881).

Reactions.—1. Brucine (60 g.) heated with alcohol (600 c.c.) and NaOH (30 g.) at 100° for 12 hours forms a solution which, after neutralisation with CO_2, filtration and evaporation, leaves a varnish containing some crystals. The crystals (7 g.) separated from the varnish by washing with water and purified by solution in very little dilute HCl and ppn. by NH_3 are thrown down as microscopic crystals of $C_{21}H_{24}N_2O_5$ (2½ g.). This gives a yellow colour with HNO_3; a pp. with bromine, and on boiling a magenta colour. An ammoniacal solution turns purple in air and finally green (Shenstone).—2. HNO_3 (S.G. 1·2 to 1·4) forms a red solution, producing 'cacotheline' $C_{21}H_{22}N_4O_9$, oxalic acid, and methyl nitrite (Strecker, *A.* 91, 76; Hanssen, *B.* 20, 451). $K_2Cr_2O_7$ and H_2SO_4 oxidise cacotheline to $C_{16}H_{18}N_2O_4$, which is also formed by the oxidation of brucine.—3. Brucine (1 mol.) heated with HCl at 140° gives off MeCl (between 1 and 2 mols.). Brucine is therefore possibly $C_{21}H_{20}(OMe)_2N_2O_2$, strychnine being $C_{21}H_{20}(OH)_2N_2O_2$ (Shenstone, *C. J.* 43, 101; *cf.* Hanssen, *B.* 17, 2266).—4. Yields on distillation with *potash* several pyridine bases. Amongst others (β)-di-methyl pyridine and (β)-tri-methyl-pyridine, quinolin tetrahydride, together with probably a di-methyl-pyridine (Oechsner de Coninck, *A. Ch.* [6] 27, 507; *C. R.* 99, 1077; *Bl.* [2] 42, 100).—5. Distilled *in vacuo* with zinc-dust it yields carbazol (Lœbisch a. Schoop, *M.* 7, 613).—6. Alkaline $KMnO_4$ gives off about half the nitrogen in the free state (Wanklyn a. Chapman, *C. J.* 21, 161).—7. ICl forms a light flocculent pp. in solutions of salts of brucine (Dittmar).

Salts.—B′HCl: crystalline tufts, m. sol. water.—$B'HClHgCl_2$: long needles (from alcohol).—$B'_2H_2PtCl_6$: yellow pp.—B′HI aq: rectangular laminæ or very short prisms; m. sol. hot water.—$B'HI_3$: brown violet needles (Jörgensen, *A. Ch.* [4] 11, 114; *J. pr.* [2] 3, 160).—$B'_2H_2I_4$: unstable orange needles.—$B'HNO_3$ 2aq: four-sided prisms; less soluble in water than strychnine nitrate. $B'_2H_2SO_4$ 7aq: long needles, v. sol. water, sl. sol. alcohol.—$B'_2H_2S_2O_3$ 5aq; S. 1 at 15° (How, *N. Ed. P. J.* [new] 98).—$B'_2H_2S_6$ 6aq: [125°]; insoluble yellow needles, formed by atmospheric oxidation of an alcoholic solution containing H_2S (Schmidt, *A.* 180, 296; *B.* 8, 1267; 10, 838, 1288).—$B'_3H_4S_{12}$.—$B'_2H_3PO_4$ *x*aq (Anderson, *P. M.* [3] 33, 163).—$B'_4H_4FeCy_6$ 2aq: hygroscopic needles, m. sol. hot water (Brandis, *A.* 66, 266). $B'_4H_4FeCy_6$ 4aq.—$B'H_4FeCy_6$: white powder (Holst a. Beckurts, *Ar. Ph.* [3] 25, 313).—$B'_3H_3FeCy_6$ 6aq.—$B'_3H_3CoCy_6$ 10aq (Lee, *Am. S.* [2] 2, 44).—$B'_2H_2NiCy_4$ (L.).—B′HCyS: scales, sol. water.—**Periodate**: needles (Bödeker, *A.* 71, 64; Langlois, *A. Ch.* [3] 34, 278).—**Nitroprusside**: S. ·15 at 15° (Davy, *Ph.* [3] 11, 756).—**Acetate**: crystalline, but gummy if impure (Shenstone).—**Dextro-tartrates**: $B'_2C_4H_6O_6$ 5½aq,—$B'_2C_4H_6O_6$ 8aq, $B'C_4H_6O_6$.—**Lævo-tartrates**: $B'_2C_4H_6O_6$ 11aq, $B'C_4H_6O_6$ 5aq (Pasteur, *A. Ch.* [3] 38, 472),—$B'C_4H_4(SbO)O_6$ (Stenhouse, *A.* 129, 26).

Methylo-iodide B′MeI 8aq: laminæ (from water); resinified by boiling KOH (Stahlschmidt, *P.* 108, 513).—$B'MeI_3$.—$B'MeI_5$.—*Methylo-bromide* B′MeBr 2½aq.—*Methylo-chloride* B′MeCl 5aq: v. sol. water and alcohol.—$B'_2Me_2PtCl_6$.—$B'HAuCl_4$.—*Methylo-sulphate* $B'_2Me_2SO_4$ 8aq: radiate crystalline mass, v. sol. water. $B'Me_2SO_4$ 2aq.—*Methylo-nitrate* $B'MeNO_3$ 2aq. The physiological action of these salts has been studied by Crum Brown (*T. E.* 25).

Ethylo-iodide B′EtI ½aq: not decomposed by KOH but converted by moist Ag_2O into a very soluble alkaline hydroxide:—$B'EtI_3$.—$B'EtI_5$ aq.—*Ethylo-platino-chloride* $B'_2Et_2PtCl_6$. Silky needles (Gunning, *J. pr.* 67, 46).

Bromo-ethylo-bromide $B'C_2H_4Br_2$ 3aq: from brucine and ethylene bromide at 100°; forms furcate groups of nacreous laminæ (from water). $AgNO_3$ pps. half the Br. Moist Ag_2O

forms the *vinylo-hydroxide* $B'C_2H_3OH$ which is strongly alkaline; two of its salts are $B'_2(C_2H_3Cl)_2PtCl_4$ and $B'C_2H_3SO_4H$ 3aq.—*Bromo-ethylo-platinochloride* $B'_2(C_2H_4Br)_2PtCl_6$ (Schad, *A.* 118, 207).

Allylo-iodide $B'C_3H_5I$ aq. — $B'C_3H_5I_3$.— $B'C_3H_5I_5$ aq. — *Allylo-platino-chloride* $B'_2(C_3H_5Cl)_2PtCl_4$. — *Isoamylo-chloride* $B'C_5H_{11}Cl$ aq. — $B'_2(C_5H_{11})_2PtCl_6$.— *Isoamylo-iodides* $B'C_5H_{11}I_3$.—$B'C_5H_{11}I_5$.

Bromo-brucine $C_{23}H_{25}BrN_2O_4$. Formed by adding an alcoholic solution of Br to an aqueous solution of brucine sulphate. Small needles (Laurent, *A. Ch.* [3] 24, 314; *cf.* Beckurts, *B.* 18, 1238).

Nitro-brucine $C_{23}H_{25}(NO_2)O_4N_2$. Formed by nitration of brucine-methylo-iodide suspended in absolute alcohol. Large red trimetric crystals. Carbonises at about 240° without melting; sol. water. Salts.—$B'HNO_3$: glistening yellow needles, v. sol. water, sl. sol. alcohol and ether.—$B'_2H_2Cl_2PtCl_4$: fine yellow needles (Hanssen, *B.* 19, 520).

Amido-brucine $C_{23}H_{25}(NH_2)O_4N_2$. Formed by reduction of nitro-brucine with tin and HCl. V. sol. water. Not isolated. Fe_2Cl_6 produces a green colouration changing to brown. Very dilute $K_2Cr_2O_7$ produces a fugitive blue-violet colour. Strong HNO_3 gives a yellow solution which is turned red by $SnCl_2$.—$B'''H_3Cl_3$: colourless prisms.—$B'''_2H_6Cl_6Pt_3Cl_{12}$x: yellow amorphous pp. (Hanssen, *B.* 19, 523).

Dinitro-brucine $C_{23}H_{24}(NO_2)_2O_4N_2$. Prepared by the action of HNO_3 on an alcoholic solution of brucine. Red amorphous powder. V. sol. water, sl. sol. alcohol, insol. ether. — $(B'HCl)_2PtCl_4$: yellow pp. (Claus a. Röhre, *B.* 14, 765).

BRYONIN $C_{48}H_{80}O_{19}$. An amorphous bitter substance in the root of the red-berried bryony (*Bryonia dioïca*) from which it may be extracted by boiling water. It appears to be resolved by dilute H_2SO_4 into glucose and two amorphous bodies, bryoretin $C_{21}H_{35}O_7$ sol. ether, and hydro-bryoretin $C_{21}H_{37}O_8$ insol. ether (Brandes a. Firnhaber, *Brandes' Ar. Ph.* 3, 356; Walz, *C. C.* 1859, 5).

BUCHU. The leaves of several species of *Barosma* growing at the Cape contain a volatile oil and a crystalline substance [85°] (Flückiger, *Ph.* [3] 4, 689; Jones, *Ph.* [3] 9, 673).

BURETTE *v.* ANALYSIS, p. 248.

BUTALANINE *v.* AMIDO-BUTYRIC ACID.

***n*-BUTANE** C_4H_{10} *i.e.* $CH_3.CH_2.CH_2.CH_3$. *Diethyl. Methyl-propyl. Butyl-hydride.* Mol. w. 58. (1°) (Butlerow, *Z.* 1867, 363). S.G. ^{0} ·60. V.D. 2·11 (calc. 2·01) (Ronalds, *C. J.* 18, 54; Pelouze a. Cahours, *A. Ch.* [4] 1, 5). S. (gas in alcohol) 18 at 14°. Occurs in petroleum (R.). Formed by the action of Zn on EtI at 150° (Frankland, *A.* 77, 221; Schöyen, *A.* 130, 233). Also, together with butylene, by heating butyl alcohol with $ZnCl_2$ (Wurtz, *A.* 93, 112). Prepared by the action of sodium-amalgam on EtI (Löwig, *J.* 1860, 397).

Iso-butane $(CH_3)_3CH$. *Trimethyl-methane, Secondary butane.* (−17°). H.F. p. 42,450. H.F. v. 40,180 (*Th.*). Prepared by slowly pouring *tert*-butyl iodide into water containing zinc, the equation being $2(CH_3)_3CI + H_2O + Zn_2 = 2(CH_3)_3CH + ZnO + ZnI_2$. Also from iso-butyl iodide and Al_2Cl_6 at 120° (Köhnlein, *B.* 16, 562). Colourless gas. Chlorine converts it into $(CH_3)_3C.Cl$ (Butlerow, *A.* 144, 10). Br at 100° forms di-bromo-butane (Carius, *A.* 126, 195). Excess of Br at 300° forms C_2Br_4 (Merz a. Weith, *B.* 11, 2244).

BUTANE CARBOXYLIC ACID *v.* BUTYRIC ACID.

Butane di-carboxylic acid *v.* PROPYL-MALONIC ACID, ISO-PROPYL-MALONIC ACID, METHYL ETHYL-MALONIC ACID, ETHYL-SUCCINIC ACID, two DI-METHYL-SUCCINIC ACIDS, ADIPIC ACID, α-METHYL-GLUTARIC ACID, and β-METHYL-GLUTARIC ACID.

Butane $\alpha\omega\omega$-**tricarboxylic acid** $C_7H_{10}O_6$ *i.e.* $MeCH_2CH(CO_2H)CH(CO_2H)_2$. *Ethyl-ethenyl-tri-carboxylic acid.* [119°]. Got by saponifying the ether with alcoholic potash (Polko, *A.* 242, 115). White rhombic crystals. V. e. sol. water, alcohol, ether, acetone, v. sol. chloroform.—Salts.—A'''_2Ba_3, insol. water and alcohol.—$A'''Ag_3$ 1½aq, sl. sol. water.—A'''_2CaH_4, insol. alcohol, v. sol. water.—$A'''CaH$ 2½aq.—A'''_2Ca_3, hygroscopic.—A'''_2Zn_3 6aq, v. e. sol. water, insol. alcohol.—A'''_2Sr_3 6aq.

Ethyl ether $MeCH_2CH(CO_2Et)CH(CO_2Et)_2$. (276°). (189° at 60 mm.). S.G. $\frac{17}{17}$ 1·065. Formed by acting on sodium malonic ether with α-bromo-butyric ether in alcoholic solution (P.).

Butane $\alpha\alpha\beta$-**tri-carboxylic acid** $CH_3.CH(CO_2H).C(CO_2H)_2.CH_3$. *Butenyl-tri-carboxylic acid.* [157°]. V. sol. water, alcohol and ether. On warming it yields *s*-di-methyl-succinic anhydride [87°] (Bischoff a. Rach, *A.* 234, 54). Salts.—$Ba_3A'''_2$.—$Ca_3A'''_2$.

Ethyl ether Et_3A'''. (c. 190°) at 50–60 mm.; (273°–275°) at ordinary pressure. Liquid. Formed by the action of α-bromo-propionic ether upon sodio-methyl-malonic ether. By boiling with HCl it is converted into *s*-di-methyl-succinic acid [189°] (Leuckart, *B.* 18, 2346).

Iso-butane tri-carboxylic acid $Me_2C(CO_2H)CH(CO_2H)_2$. [120°]. Prepared by saponifying the ether with alcoholic potash (Barnstein, *A.* 242, 128). Needle-shaped crystals (from water). V. e. sol. water, alcohol, ether, acetone, v. sl. sol. chloroform, benzene, petroleum ether, carbon disulphide. Decomposed by boiling with water, giving off CO_2. Salts.—K_3A''' 2aq. Quadratic prisms: v. e. sol. water, insol. alcohol.—$Ca_3A'''_2$ 9aq: m. sol. water. —CaA'''_2 2aq: v. e. sol. water.—$Sr_3A'''_2$ 7aq.

Ethyl ether Et_3A'''. (181°–185°) at 30–40 mm.; (279°–281°) at ordinary pressure (L.); (273°) (B.). S.G. $\frac{17}{17}$ 1·064. Liquid. Formed by the action of α-bromo-isobutyric ether upon sodio-malonic ether. By boiling with HCl it is converted into *u*-di-methyl-succinic acid [139°] (Leuckart, *B.* 18, 2350; Barnstein, *A.* 242, 126).

Butane $\omega\omega\gamma\gamma$-**tetra-carboxylic ether** $C_{16}H_{26}O_8$ *i.e.* $(CO_2H)_2.CH.CH_2.CH_2.CH(CO_2H)_2$. (275°–280°) at 225 mm. Formed, together with trimethylene dicarboxylic acid, by the action of ethylene bromide on sodium malonic ether (Perkin, jun., *C. J.* 51, 17; *B.* 19, 2038). The yield is very small. The corresponding acid splits up when heated into CO_2 and adipic acid. By treatment with sodium ethylate it gives a di-sodio-derivative which by the action of bromine yields tetra-methylene-tetra-carboxylic ether $\begin{matrix} CH_2.C(CO_2Et)_2 \\ | \quad\quad | \\ CH_2.C(CO_2Et)_2 \end{matrix}$.

Iso-butane tetra-carboxylic ether $(CO_2Et)_2CH.CHMe.CH(CO_2Et)_2$. (c. 211°) at 20 mm. A by-product in the preparation of ethylidene-malonic ether from aldehyde and malonic ether; it is formed by the addition of malonic ether to ethylidene-malonic ether $CH_3.CH:C(CO_2Et)_2$ (Komnenos, *A.* 218, 158; Claisen, *J. pr.* [2] 35, 414). The corresponding acid is split up by distillation into CO_2 and β-methyl-glutaric acid $CO_2H.CH_2.CHMe.CH_2.CO_2H$.

Butane $\alpha\alpha\beta\beta$-tetra-carboxylic ether $(CO_2Et)_2CMe.CMe(CO_2Et)_2$. *Di-methyl-acetylene-tetra-carboxylic ether.* S.G. $\frac{15}{15}$ 1·114. From sodio-methyl-malonic ether by the action of [illegible] of chloro-methyl-malonic ether. From sodio-ethane tetra-carboxylic ether and MeI (Bischoff a. Rach, *B.* 18, 1202; *A.* 234, 70).

Butane tetra-carboxylic ether $CH(CO_2H)_2.C(C_2H_5)(CO_2Et)_2$. *Ethyl-acetylene-tetra-carboxylic acid.* Thick colourless oil; formed by the action of chloro-malonic ether on sodio-ethyl-malonic ether (Bischoff a. Rach, *B.* 17, 2785).

Butane hexa-carboxylic ether $CO_2Et.CH_2.C(CO_2Et)_2.C(CO_2Et)_2.CH_2.CO_2Et$. [57°]. Six-sided tables. From sodium ethane tri-carboxylic ether $(CO_2Et)_2CNa.CH_2.CO_2Et$ by the action of iodine or of $(CO_2Et)_2CCl.CH_2.CO_2Et$ (Bischoff, *B.* 16, 1046; 17, 2786).

ISO-BUTANE SULPHINIC ACID $(CH_3)_2CH.CH_2.SO_2H$. From iso-butane sulpho-chloride by zinc-dust (Pauly, *B.* 10, 942). Liquid. Reduced by nascent hydrogen to iso-butyl mercaptan.—ZnA'_2. Plates (from alcohol).

***n*-BUTANE SULPHONIC ACID** $C_4H_9SO_3H$. Formed by the action of HNO_3 on *n*-butyl mercaptan (Grabowsky, *A.* 175, 341). Thick syrup, v. sol. water and alcohol, m. sol. ether.—AgA': plates.—PbA'_2: plates, sl. sol. alcohol.—$PbA'_2,2Pb(OH)_2$: crystalline powder, sl. sol. water.—BaA'_2aq: plates.—$CaA'_2, 2aq$.—NaA': plates.

Iso-butane sulphonic acid $(CH_3)_2CH.CH_2.SO_3H$. From iso-butyl mercaptan and HNO_3 (Mylius, *B.* 5, 978). Syrup. Its salts are v. sol. water.—AgA': scales.—BaA'_2: needles.

Chloride $C_4H_9SO_2Cl$ (190°) (Pauly, *B.* 10, 942).

ISO-BUTENYL ACETATE $CH_2:CMe.CH_2OAc$ (120°) (Scheschukoff, *J. R.* 16, 502).

BUTENYL ALCOHOL C_4H_8O *i.e.* $CH_3.CH:CH.CH_2OH$. (117°). A product of the action of iron and acetic acid upon crotonic and tri-chloro-butyric aldehydes (Lieben a. Zeisel, *M.* 1, 825). HI gives $CH_3.CH_2.CHI.CH_3$.

Isobutenyl alcohol $CH_2:CMe.CH_2OH$. (113°). S.G. $\frac{0}{}$ ·8695. Formed by boiling isobutenyl chloride with very dilute K_2CO_3 (Scheschukoff, *J. R.* 16, 499). Dilute H_2SO_4 changes it to iso-butyric aldehyde. HI forms *tert*-butyl iodide.

Ethyl ether $CH_2:CMe.CH_2OEt$ (78°–85°). From isobutenyl chloride and KOEt.

***Sec*-isobutenyl alcohol** $CMe_2:CH.OH$.

Methyl ether $CMe_2:CH.O.Me$. *Methyl isocrotyl oxide.* (70°–74°). From bromo-iso-butylene and NaOMe at 140°. Dilute H_2SO_4 at 140° gives HOMe and isobutyric aldehyde (Eltekoff, *B.* 10, 705; *J. R.* 9, 163).

Ethyl ether $CMe_2:CH.OEt$. (93°). Similarly prepared (E.; S.; Butlerow, *Z.* 1870, 521).

BUTENYL-TRI-AMINE $CH(CH_2NH_2)_3$. (above 150°). From the nitrile of methane tri-carboxylic acid $CH(CN)_3$, tin, and HCl.—$B'_23H_2PtCl_6$ (Fairlie, *C. J.* 16, 362).

BUTENYL-BENZENE *v.* PHENYL-BUTYLENE.

BUTENYL CHLORIDE *v.* CHLORO-BUTYLENE.

(α)-BUTENYL-CUMENE $C_6H_4PrC_4H_7$. *Iso-propyl-butenyl-benzene.* (243°). S.G. ·8875. Obtained from bromo-cumyl-valeric acid $C_6H_4Pr.CH_2.CBrEt.CO_2H$ and Na_2CO_3Aq (Perkin, *C. J.* 32, 662). Forms a dibromide [77°].

(β)-Butenyl-cumene $C_6H_4Pr.C_4H_7$. (235°). S.G. $\frac{15}{}$ ·889. Cuminic aldehyde (10 g.) sodic isobutyrate (5 g.) and isobutyric anhydride (15 g.) are heated together. The oily product is distilled with water and then over solid KOH and Na (Perkin, *C. J.* 35, 141). It forms a liquid dibromide.

BUTENYL-GLYCERIN *v.* TRI-OXY-BUTANE.

DI-BUTENYL-KETONE *v.* DI-ALLYL-ACETONE (p. 134).

***o*-BUTENYL-PHENOL.**

Methyl ether [2:1] $MeO.C_6H_4.CH:CH.CH_2.CH_3$. (233°). S.G. $\frac{15}{15}$ ·9817; $\frac{30}{30}$ ·9740. From the methyl derivative of oxy-phenyl-angelic acid by successive treatment with HI and Na_2CO_3Aq (Perkin, *C. J.* 33, 213). Oil. Combines with bromine. Forms a red solid with H_2SO_4.

***p*-Butenyl-phenol.** *Methyl ether* [4:1] $MeO.C_6H_4.C_4H_7$. [17°]. (243°). S.G. $\frac{20}{}$ ·973. Prepared like the preceding (Perkin, *C. J.* 32, 671).

***o*-Iso-butenyl-phenol** $C_{10}H_{12}O$ *i.e.* $C_4H_7.C_6H_4.OH$. (223°–225°). S.G. $\frac{15^{\circ}}{}$ 1·017. Salicylic aldehyde (30 g.) sodic isobutyrate (22 g.) and isobutyric anhydride (45 g.) are heated together for 4 hours. Water is added to the product, and the oily butenyl-phenyl isobutyrate saponified by alcoholic KOH. The alcohol is boiled off, dilute HCl is added and the oil which separates is distilled (Perkin, *C. J.* 35, 142). *Properties.*—Oil, with smoky and cedar-like odour. Sol. potash but insol. NH_3. With salicylic aldehyde and conc. H_2SO_4 it forms a purple solution.

***p*-Iso-butenyl-phenol** $C_{10}H_{12}O$ *i.e.* $C_4H_7.C_6H_4.OH$. (230°–235°). From *p*-oxy-benzoic aldehyde, sodic isobutyrate and butyric anhydride. Yield small (Perkin, *C. J.* 35, 145). An oil which solidifies in a freezing mixture.

Methyl ether $C_4H_7.C_6H_4.OMe$. [9°]. (237°). From anisic aldehyde (20 g.), sodic isobutyrate (15 g.) and isobutyric anhydride (30 g.) by boiling at 180°. The product is distilled with steam and the oil dried over K_2CO_3. Cooled by ice and HCl it solidifies. On oxidation it yields anisic and acetic acid.

ω-BUTENYL-STYRENE $C_6H_5.CH:CH.C_4H_7$. (245°–248°). *Phenyl hexinene.* Cinnamic aldehyde (10 g.), sodium isobutyrate (15 g.) and isobutyric anhydride (10 g.) are heated together for two hours. CO_2 comes off, and the residue is distilled with steam, washed with NH_3, dried and rectified over Na (Perkin, *C. J.* 35, 141).

Properties.—Lighter than water. Rapidly oxidises in air, becoming a resin. It combines with bromine.

***Iso*-BUTENYL-TOLYLENE-*o*-DIAMINE** $C_{11}H_{14}N_2$ *i.e.* $C_7H_6\!<\!{NH \atop N}\!>\!C.C_3H_7$. [158°].

Formed, together with a small quantity of tolu-butyraldehydine $C_7H_6<\begin{matrix}N:CH.C_3H_7\\N:CH.C_3H_7\end{matrix}$, by shaking a cold acetic acid solution of tolylene-*o*-diamine (1 mol.) with an aqueous or alcoholic solution of butyric aldehyde (2 mols.). Small colourless needles. V. sol. alcohol and ether, sl. sol. water. Very bitter taste (Hinsberg, *B.* 20, 1589).

BUTINENE C_4H_6 *i.e.* $CH_2:CH.CH:CH_2$. *Erythrene. Vinyl-ethylene. Pyrrolylene.* Occurs in the liquid got by compressing coal-gas (Caventou, *B.* 6, 70; Grimaux a. Cloez, *C. R.* 104, 118). Formed also (?) by passing fusel oil through a red-hot tube (Caventou, *A.* 127, 93). Obtained by boiling erythrite with conc. formic acid (5 pts.) (Henninger, *B.* 6, 70); and by the action of KOH on di-methyl-pyrrolidine methylo-iodide (Ciamician a. Magnaghi, *B.* 19, 569). A gas. It forms a tetrabromide [119°]. Pyrrolylene and the butinene from erythrite form also a second tetrabromide [40°] so that they are probably mixtures of two butinenes.

Butinene $CH_3.CH_2.C:CH$. *Ethyl-acetylene Crotonylene.* (18°). From methyl ethyl ketone by successive treatment with alcoholic KOH and PCl_5 (Bruylants, *B.* 8, 412). Gives a white pp. in ammoniacal $AgNO_3$ and a yellow pp. in ammoniacal cuprous chloride. Mercuric chloride solution gives a pp. of $(C_4H_6)_2(HgOHgCl_2)_3$ (Kutscheroff, *B.* 17, 24), whence HCl produces methyl ethyl ketone. The same butinene appears to be formed when a mixture of acetylene and ethylene is passed through a red hot tube. It forms a tetrabromide [113°] (Berthelot, *A. Ch.* [4] 9, 406; Prunier, *Bl.* 20, 72; *A. Ch.* [5] 17, 17; *C. R.* 76, 1410).

Butinene $CH_3.C:C.CH_3$(?). *Crotonylene.* (18°). From crude butylene bromide and alcoholic KOH (Caventou, *A.* 127, 347). From *αβ*-di-bromo-butane and alcoholic KOH (Almedingen, *J. R.* 13, 392). Also formed by distilling barium acetate with S (Pfankuch, *J. pr.* [2] 6, 110). H_2SO_4 (3 mols.) diluted with water (1 mol.) converts it into hexa-methyl-benzene.

Butinene C_4H_6. *Caoutchin.* [−10°]. (15°). S.G. $\frac{-2}{}$ ·65. Formed by the dry distillation of caoutchouc (*q.v.*) (Bouchardat, *A.* 27, 33).

BUTINENE GLYCOL *v.* Di-oxy-butylene.

BUTONENE-AMIDO-PHENYL MERCAPTAN $C_{16}H_{12}N_2S_2$ *i.e.*

$$C_6H_4<\begin{matrix}N\\S\end{matrix}>C.CH_2.CH_2.C<\begin{matrix}N\\S\end{matrix}>C_6H_4. \qquad [137°].$$

From amido-phenyl-*o*-mercaptan and succinamide (Hofmann, *B.* 13, 1231). Needles (from alcohol).—$B'HAuCl_4$.

BUTYL DERIVATIVES of hydroxylic compounds are described under the compounds of which they are the ethers.

DI-BUTYL *v.* Octane.

BUTYL ACETATE $C_6H_{12}O_2$ *i.e.* $C_4H_9.OAc$. (124·5°). S.G. $\frac{0}{0}$ ·9016. C.E. (0°–10°) ·00113. S.V. 150·6 (Gartenmeister, *A.* 233, 259). From butyl iodide and AgOAc (Lieben a. Rossi, *A.* 158, 170; Linnemann, *A.* 161, 193; Pribram a. Handl, *M.* 2, 693).

Isobutyl acetate $(CH_3)_2CH.CH_2.OAc$. V.D. 4·073 (calc. 4·017). (116·3°) (Elsässer, *A.* 218, 326); (117° cor.) (Perkin, *C. J.* 45, 495; (112·8°) (R. Schiff, *A.* 220, 109). S.G. $\frac{0}{4}$ ·8921 (E.); $\frac{15}{15}$ ·8774; $\frac{25}{25}$ ·8688 (P.). C.E. (0°–10°) ·001137 (E.). M.M. 6·623 at 10°. S.V. 150·10 (E.); 152·5 (S.). Formed from isobutyl iodide and AgOAc, or by distilling potassium isobutyl sulphate with KOAc (Wurtz, *A.* 90, 121).

Sec-**Butyl acetate** $CH_3.CH_2.CH(OAc).CH_3$. (112°). S.G. $\frac{0}{}$ ·892. From *sec*-butyl iodide and AgOAc (De Luynes, *J.* 1864, 501; Lieben, *A.* 150, 112).

Tertiary **Butyl acetate** $(CH_3)_3C.OAc$. (93°–96°). From the iodide and AgOAc. Readily saponified by baryta-water (Butlerow, *A.* 144, 7).

ISO-BUTYL-ACETIC ACID *v.* Hexoic acid.

ISOBUTYL-ACETO-ACETIC ETHER *v.* p. 24.

BUTYL-ACRIDINE $C_{17}H_{17}N$ *i.e.*

$$C_6H_4<\begin{matrix}C(C_4H_9)\\ | \\ N\end{matrix}>C_6H_4.$$

From valeric acid (30 g.), di-phenylamine (30 g.) and $ZnCl_2$ (50g.) heated gradually for 20 hours up to 220° (Bernthsen a. J. Traube, *A.* 224, 41; *B.* 17, 1508).

Salts.—B'HCl [191°]: yellow columns, v. sol. water or alcohol, very dilute solutions show blue fluorescence. Insol. ether.—$B'HNO_3$ [139°].—$B'H_2CrO_4$ [c. 100°].

Dihydride $C_{13}H_{10}N(C_4H_9)$. [98°–100°]. Got by reducing the hydrochloride with zinc-dust. White plates (from alcohol).

BUTYLACTIC ACID *v.* Oxy-butyric acid.

BUTYLAL *v.* Butyric aldehyde.

BUTYL ALCOHOL $C_4H_{10}O$. Mol. w. 74. The four butyl alcohols indicated by theory are known.

n-**Butyl-alcohol** $CH_3.CH_2.CH_2.CH_2OH$. (117° cor.). S.G. $\frac{0}{0}$ ·8233 (Zander, *A.* 224, 79); $\frac{20}{4}$ ·8096 (Brühl, *A.* 203, 16). S. 8·3. C.E. (0°–10°) ·00087 (Z.). μ_β 1·4040. S.V. 101·6 (Schiff, *A.* 220, 101). R_∞ 35·45 (B.). *Critical point* 287° (Paulewsky, *B.* 16, 2634).

Occurrence.—In the heavy oils from brandy. It is completely absent from the products of the fermentation of sugar with elliptical yeast (Claudon a. Morin, *C. R.* 104, 1187).

Formation.—1. From butyryl chloride, butyric acid and sodium-amalgam (Saytzeff, *J. pr.* [2] 3, 76).—2. By the fermentation of glycerin by a *Schizomycetes* or by certain *Bacteria* in presence of $CaCO_3$ and ammonium tartrate; *n*-butyric acid and a little alcohol are formed at the same time (Fitz, *B.* 9, 1348; Vigna, *B.* 16, 1438).—3. A product of the reduction of butenyl alcohol (Lieben a. Zeisel, *M.* 1, 825).

Preparation. — From butyric aldehyde, water, and sodium-amalgam (Lieben a. Rossi, *C. R.* 68, 1561; 78, 1561; *A.* 151, 121; 158, 137; 165, 145; *C. J.* 24, 516; Linnemann, *A.* 161, 179).

Properties.—Liquid. Separated by $CaCl_2$ from aqueous solution. On oxidation it produces butyric acid. Fused $ZnCl_2$ forms the two *n*-butylenes (Le Bel a. Greene, *C. R.* 89, 413).

Combination.—$(C_4H_{10}O)_3CaCl_2$ (Heindl, *M.* 2, 200).

Iso-butyl alcohol $(CH_3)_2CH.CH_2OH$. (106·6°–106·8°) at 763·2 mm. (R. Schiff, *A.* 220, 102) (108°) (Linnemann, *A.* 160, 238). S.G. $\frac{20}{4}$ ·8062 (Brühl); $\frac{15}{15}$ ·8069; $\frac{25}{25}$ ·8009 (P.). S. 9·5 at 18°. S.V. 101·63. H.F. p. 71,150. H.F. v. 68,580 (*Th.*). μ_β 1·4007. R_∞ 35·41. M.M. 4·936 at 17·7°.

Occurrence.—In fusel oil from beet or potatoes and other sources (Wurtz, *A. Ch.* [3] 42, 129; *A.* 85, 197; 93, 107; *C. R.* 35, 310).

......yl angelate and isobutyrate occur in Roman oil of chamomile (Köbig, *A.* 195, 96).

Formation.—1. Isobutylene combines with ClOH forming $(CH_3)_2$:CCl.CH_2OH, which is reduced by sodium amalgam and water (Butlerow, *A.* 144, 24).—2. Isobutyl alcohol is produced by the action of *Bacillus butylicus* upon sugar, glycerin, &c., even in presence of 8 p.c. alcohol (Ordonneau, *C. R.* 102, 219; Claudon a. Morin, *C. R.* 104, 1187).

Properties.—Liquid; smelling like fusel oil; separated from its aqueous solution by $CaCl_2$. The rate of etherification has been studied by Menschutkin (*A. Ch.* [5] 23, 14).

Reactions.—1. CrO_3 produces isobutyric, acetic, carbonic acids, and acetone (Krämer, *B.* 7, 252; Schmidt, *B.* 7, 1361).—2. Distilled over *zinc-dust* splits up into isobutylene and H_2O (Jahn, *B.* 13, 989).—3. Dropped upon fused $ZnCl_2$ it forms isobutylene and CH_3.CH:CH.CH_3 (Le Bel a. Greene, *Am.* 2, 23). 4. Heated with ammoniacal $ZnCl_2$ at 260°–280° it yields a mixture of mono-, di- and tri- isobutylamine (the latter in smaller quantity), the yield of mixed bases amounting to 50 to 70 p.c. of the alcohol used (Merz a. Gasiorowski, *B.* 17, 623).

Combinations.—$(C_4H_{10}O)_3CaCl_2$ (Heindl, *M.* 2, 208).

Metallic derivatives. — KOC_4H_9. — $NaOC_4H_9(C_4H_{10}O)_3$ (De Forcrand, *C. R.* 104, 169).—$Al_2(OC_4H_9)_6$. [140°]. S.G. $\frac{4}{4}$ ·9825 (Gladstone a. Tribe, *C. J.* 39, 6). From Al (1 g.), iodine (2 g.) and isobutyl alcohol 40 c.c. at 100°. The yield is good (16 g.). Once fused it remains long fluid at 70°.

Secondary butyl alcohol

$CH_3.CH_2.C(CH_3)H.OH$. *Methyl-ethyl-carbinol. Butylene hydrate.* (99°) at 740 mm. S.G. ^{0} ·827 (Lieben, *A.* 150, 114).

Formation. — 1. From *n*-butylamine by nitrous acid; at the same time some *n*-butyl alcohol is also formed (Linnemann a. Zotta *A.* 162, 3; Meyer, *B.* 10, 130).—2. By treating the compound of HClO with isobutylene, CH_3.CHCl.CH(OH).CH_3, with sodium amalgam (Lieben, *A.* 151, 121).—3. By the action of zinc ethide on glycolic iodhydrin (Butlerow a. Ossokin, *A.* 145, 263).—4. Symmetrical dichloro-diethyl oxide, $(CH_3.CHCl)_2O$ is converted by $ZnEt_2$ into $(CH_3.CHEt)_2O$, a butyl ether which, on treatment with HI at 130° gives secondary butyl iodide (Lieben, *A.* 141, 236; Kessel, *A.* 175, 44). 5. Zinc ethide forms a crystalline compound with aldehyde, CH_3.CHEt(OZnEt), which is decomposed by water into secondary butyl alcohol, ethane, and $Zn(OH)_2$. (Wagner, *J. R.* 8, 37; *A.* 181, 261).—6. From formic ether by treating with a mixture of $ZnEt_2$ and $ZnMe_2$ and decomposing the product with water (Kanonnikoff a. Saytzeff, *A.* 175, 374).

Preparation.—Secondary butyl iodide (*q.v.*) is treated with silver acetate and the product saponified by potash (De Luynes, *A.* 128, 330; 132, 274).

Properties.—Liquid with strong odour, ppd. from aqueous solution by K_2CO_3.

Reactions.—1. *Oxidises* to methyl-ethyl-ketone and acetic acid (Saytzeff, *Z.* 6, 327).—2. The pure alcohol is unaltered when *heated* at 240°–250° during 8 to 16 hours in a sealed tube, but the presence of a trace of HCl, HBr, or especially HI, is sufficient to split it up, forming pseudobutylene. The reaction commences at 220° and is complete in 5 or 6 hours (Bougaieff a. Wolkoff, *Bl.* [2] 45, 9).

Tertiary butyl alcohol $(CH_3)_3C.OH$. *Tri-methyl-carbinol.* [25°] (83° cor.). S.G. ^{27} ·779 (Linnemann); ^{30} ·7 (Butlerow); $\frac{20}{}$ ·786; $\frac{20}{4}$ ·780 (Brühl); $\frac{1}{15}$ ·7836; $\frac{25}{}$ ·7761 (Perkin). M.M. 5·122 at 24·3°. μ 1·3924. R_∞ 35·53. *Critical point* 235° (Pawlewski, *B.* 16, 2634).

Formation.—1. Zinc methide (2 mols.) and acetyl chloride (1 mol.) mixed at 0°, form, after some hours, a crystalline compound, CH_3.CMe(OZnMe)Me, which is decomposed by water into tertiary butyl alcohol, $Zn(OH)_2$ and CH_4 (Butlerow, *A.* 144, 1; Wagner a. Saytzeff, *A.* 175, 361; Pawloff, *A.* 188, 118).—2. Together with isobutyl alcohol by treating isobutyl iodide with acetic acid and Ag_2O (Linnemann, *A.* 162, 12; Butlerow, *A.* 168, 143).—3. From isobutylamine and HNO_2.—4. From isobutyl cyanate and KOH (Linnemann, *A.* 162, 12).—5. From tertiary butyl iodide (*q.v.*) and water, even in the cold (Dobbin, *C. J.* 37, 238).—6. A mixture of *iso-* and *tert-* butyl chlorides is got by heating isobutyl alcohol with HCl; when heated with water (6 vols.) at 100° the chloride of *tert*-butyl alcohol is the only one converted into its alcohol (Freund, *J. pr.* [2] 12, 25).

Preparation.—Liquid isobutylene is sealed up with twice its volume of a mixture of equal parts of water and sulphuric acid, and the contents are left till homogeneous and then distilled (Butlerow, *Z.* [2] 6 237; *A.* 180, 246).

Properties.—Trimetric prisms. Forms a hydrate $(C_4H_{10}O)_2H_2O$ which boils at 80° (Butlerow).

Reactions.—1. CrO_3 mixture gives acetone together with acetic, carbonic and a little isobutyric acid (Butlerow, *Z.* 1871, 485).—2. Heating with anhydrous $H_2C_2O_4$ produces butylene (Cahours a. Demarçay, *C. R.* 86, 991).—3. When taken internally it is excreted in the urine as butyl-glycuronic acid $C_{10}H_{18}O_7$ (Thierfelder a. Mering, *H.* 9, 514) which is decomposed by boiling dilute HCl into *tert*-butyl alcohol and glycuronic acid.

DI-ISOBUTYL ALDEHYDATE *v.* p. 105.

ISO-BUTYL ALDEHYDE *v.* ISOBUTYRIC ALDEHYDE.

ISO-BUTYL-ALDOXIM *v.* ISOBUTYRIC ALDEHYDE.

ISO-BUTYL-AMIDO-ISO-BUTYL-BENZENE $C_4H_9.NH.C_6H_4.C_4H_9$. (260°–270°). From aniline hydrochloride (10 g.) and iso-butyl alcohol (13 g.) at 230° (Studer, *A.* 211, 240; *B.* 14, 1473). Oil. Does not give the carbamine reaction.

Nitroso-derivative S.G. ^{24} ·991. Solidifies on keeping.

Acetyl-derivative. [74°]. (above 300°). Needles (from benzoline).

BUTYL-AMIDO-TOLUENE *v.* METHYL-BUTYL-PHENYL-AMINE.

n-**BUTYLAMINE** $C_4H_9NH_2$ *i.e.* $Pr.CH_2.NH_2$. Mol. w. 73. (76°). S.G. ^{0} ·755, ^{26} ·733.

Formation.—1. From butyl cyanate and KOHAq (Lieben a. Rossi, *A.* 158, 172; Meyer, *B.* 10, 131).—2. From butyronitrile by reduction

(Linnemann a. Zotta, *A.* 162, 3).—3. From nitrobutane, Sn and HCl (Züblin, *B.* 10, 2083).

Properties.—Miscible with water; dissolves freshly ppd. $Cu(OH)_2$ and Ag_2O. Reduces alkaline solutions of copper, silver, and mercury. Nitrous acid converts it into *sec*-butyl alcohol.—**Platino-chloride** $(B'.HCl)_2PtCl_4$: yellow crystalline plates, m. sol. cold water.

Primary isobutyl-amine $Pr.CH_2.NH_2$. (68°) (R. Schiff, *B.* 19, 565). S.G. $\frac{15}{}$ ·736. S.V. 106·16 (S.). H.F. p. 38,460. H.F. v. 35,560 (*Th.*).

Formation.—1. By distilling potassium isobutyl sulphate with potassium cyanate and treating the product with KOH (Wurtz, *A.* 93, 124; Linnemann, *A.* 162, 23).—2. By heating isobutyl bromide with alcoholic NH_3 and separating the mono-, di-, and tri- butylamines by oxalic ether (Reimer, *B.* 3, 756; Hughes a. Römer, *B.* 7, 511; Malbot, *C. R.* 104, 63, 228). On heating isobutyl chloride with ammonia (molecular proportions) in isobutyl alcoholic solution or in aqueous solution very nearly similar results are obtained; namely one part of mono-butylamine, four of di-, and five parts of tri-butylamines (M.).—3. Formed, together with di- and tri- isobutylamine, by heating isobutyl-alcohol with ammoniacal $ZnCl_2$ at 260°–280°; the yield of mixed bases amounts to 50–70 p.c. of the alcohol used (Merz a. Gasiorowski, *B.* 17, 623). 4. By reducing nitro-isobutane (Demole, *A.* 175, 142).—5. A mixture of equal mols. of valeramide (ordinary) and bromine is run into an excess of a 10 p.c. solution of KOH at 60°; the yield is 90 p.c. (Hofmann, *B.* 15, 769).

Salts.—B'HCl. [160°]. S. 133 at 15°.—$(B'HCl)_2PtCl_4$: microscopic rhombic tablets.—$B'HAuCl_4$.—Sulphate: cauliflower-like groups of needles, not deliquescent.

Secondary butyl-amine $CH_3.CH_2.CH(NH_2).CH_3$. (63°). From dilute H_2SO_4 and *sec*-butyl thio-carbimide (from volatile oil of scurvy-grass) (Reymann, *B.* 7, 1289). Also from the iodide or cyanate (Hofmann, *B.* 7, 513).—$B'_2H_2PtCl_6$.

Tertiary butyl-amine Me_3CNH_2 (46° cor.). S.G. $\frac{0}{}$ ·7155; $\frac{15}{}$ ·7004. C.E. (0°–7·8°) ·0014. Formed together with isobutylamine by the successive action of silver cyanate and aqueous KOH on isobutyl iodide. Colourless ammoniacal liquid, attacks indiarubber and cork. Miscible with water, but separated by K_2CO_3 or KOH from its solution (Brauner, *A.* 192, 72; *cf.* Linnemann, *A.* 162, 19; Hofmann, *B.* 7, 513).

Salts.—B'HCl melts at [270°–280°] and boils soon after. On solidifying it increases greatly in bulk.—$(B'HCl)_2PtCl_4$. Large monoclinic prisms (from alcohol).—B'HI.—$B'HNO_3$. *Sulphate*: six-sided prisms, not deliquescent.

Di-*n*-butyl-amine $(Pr.CH_2)_2NH$. (160°). Formed, together with *n*-butylamine, by treating butyl cyanate with KOH (Lieben a. Rossi, *A.* 158, 175). Converted by nitrous acid into primary and secondary *n*-butyl alcohols and *n*-butylene (Meyer, *B.* 10, 130).—$B'_2H_2PtCl_6$. *Nitroso- derivative* $(C_4H_9)_2N.NO$. (236° cor.).

Di-iso-butyl-amine $(Pr.CH_2)_2NH$. (137°). Formed, together with mono- and tri- iso-butylamine, by heating iso-butyl alcohol with ammoniacal $ZnCl_2$ at 260°–280°. The secondary amine is isolated from the mixture of bases (which amounts to 50–70 p.c. of the alcohol used) by means of its nitrosamine (Merz a. Gasiorowski, *B.* 17, 623). Prepared by heating iso-butyl iodide or bromide with alcoholic NH_3 to 150° (Ladenburg, *B.* 12, 948). Butyl iodide (1 mol.) in the cold acts upon di-isobutylamine (1 mol.) forming di-isobutylamine hydrochloride and free tri-iso-butylamine (M.).

Salts.—B'HCl: plates or scales. S. 62·5 at 15°; S. (ether) ·07 at 15°; S. (alcohol) ·06 at 14° (Malbot, *C. R.* 104, 366). — $B'_2H_2PtCl_6$. — $B'HClAuCl_3$. Yellow tables, sparingly soluble in cold water.

Nitroso- derivative $N(NO)(C_4H_9)_2$. [0°]. (213°–216°). Oil. Prepared by the action of KNO_2 on a solution of di-isobutylamine hydrochloride.

Tertiary di-butyl-amine $(C_4H_9)_2NH$ *i.e.* $(CMe_3)_2NH$. From tertiary butyl iodide and tertiary butylamine at 50°. But above 70° isobutylene is given off: $C_4H_9NH_2 + C_4H_9I = C_4H_8 + C_4H_9NH_2,HI$ (Rudnew, *Bl.* [2] 33, 299).

Salt.—B'HI. Very soluble in water and alcohol. Converted by potash, or even boiling water, into tertiary butylamine.

Tri-*n*-butyl-amine $(C_4H_9)_3N$. Mol. w. 185. (c. 213° cor.). S.G. $\frac{0}{}$ ·791; $\frac{20}{}$ ·778. From *n*-butyl iodide and NH_3 (Lieben a. Rossi, *A.* 165, 115).—$B'_2H_2PtCl_6$.

n-Butylo-iodide $(C_4H_9)_4NI$: plates (Lieben a. Rossi, *A.* 165, 113).

Tri-isobutyl-amine $(PrCH_2)_3N$. (185°). S.G. $\frac{21}{21}$ ·785 (Sachtleben, *B.* 11, 733). Formed, together with mono- and di- iso-butylamine, by heating isobutyl alcohol with ammoniacal $ZnCl_2$ at 260°–280°. The tertiary amine is isolated from the mixture of bases (yield 50–70 p.c. of the alcohol) by means of its sparingly soluble ferrocyanide (Merz a. Gasiorowski, *B.* 17, 623). Also from di-iso-butylamine and isobutyl bromide. Also from isobutyl iodide (1 mol.) and NH_3Aq (1 mol.) at 160° (Malbot, *C. R.* 105, 575). Does not mix with water. With isobutyl bromide it gives off butylene and forms tri-isobutylamine hydrobromide (Reimer, *B.* 3, 757). Isobutyl iodide (1 mol.) at 180° forms hydriodides of di- and tri-isobutylamine and butylene (M.). Isobutyl chloride (1 mol.) at 170° gives pure di-isobutylamine hydrochloride and butylene.

Salts.—B',HCl, B',HNO_3 and B'_2,H_2SO_4 are extremely soluble.—$(B'HCl)_2PtCl_4$ orange plates, sol. hot water.—$B'HClAuCl_3$: amorphous, insol. water.

Tert-**BUTYL**-*tert*-**AMYL-AMINE** $(C_4H_9)(C_5H_{11})NH$. The iodide of this base is formed by the slow action of tertiary amyl iodide on tertiary butylamine in the cold. It is very unstable, being decomposed by solution in water (?) (Rudneff, *Bl.* [2] 33, 297).

***n*-BUTYL-ANILINE** $C_{10}H_{15}N$ *i.e.* $C_6H_5.NHC_4H_9$. (235° at 720°). Colourless oily fluid. Easily volatile with steam.

Salts.—B'HCl: very soluble white needles.—$B'HNO_3$*: easily soluble.—$B'_2H_2SO_4$*: easily soluble fine white needles.

Acetyl derivative $C_6H_5.N(C_4H_9)Ac$: (274°) at 718 mm., colourless fluid.

Nitrosamine $C_6H_5.N(C_4H_9)NO$: yellow fluid; easily soluble in alcohol and ether, insoluble in water (Kahn, *B.* 18, 3365).

Isobutyl-aniline $Pr.CH_2.NHPh$. (242°) (G.); (226°) (N.). S.G. $\frac{15}{}$ ·926 (G.). From isobutyl bromide and aniline (Gianetti, *G.* 12, 268).—B'HCl.—B'HBr.—B'HI.

Acetyl derivative (267°) (Nölting, *J.* 1883, 703).

p-Nitroso-derivative

[4:1] $C_6H_4(NO).NHCH_2Pr$ or $C_6H_4<\begin{matrix}NH.CH_2Pr\\ | \quad >O\\ N\end{matrix}$

[94°]. From isobutyl-aniline, HCl, and $NaNO_2$ (Wacker, *A.* 243, 297). Steel-blue crystals, v. sol. alcohol, sl. sol. water. *Reactions.*—1. *Reduction* gives isobutyl-phenylene diamine.—2. The chloride boiled with aqueous NaOH gives iso-butyl-amine and *p*-nitroso-phenol.—3. HCl and $NaNO_2$ give a nitrosamine $C_6H_4(NO).N(NO).CH_2Pr$ crystallising in bright green plates, v. sol. alcohol and ether, insol. water.

Di-isobutyl-aniline $(PrCH_2)_2NPh$. (c. 218°). From aniline and isobutyl bromide (Studer, *A.* 211, 235).

DI-BUTYL-ANILINE-AZYLINE *v.* *Di-butyl-amido-benzene-azo-di-butyl-aniline.*

BUTYL-ANISOL *v.* *Methyl ether of* BUTYL-PHENOL.

ISO - BUTYL - ANTHRACENE $C_{18}H_{18}$ *i.e.* $C_6H_4<\begin{matrix}C(C_4H_9)\\ | \\ CH\end{matrix}>C_6H_4$ [57°]. Fluorescent needles. Prepared by the action of zinc-dust, isobutyl bromide and NaOH on anthraquinone (Liebermann a. Tobias, *B.* 14, 802; *A.* 212, 107). The *picric acid compound* forms long brownish-red needles.

Di-hydride $C_6H_4<\begin{matrix}CH(C_4H_9)\\CH_2\end{matrix}>C_6H_4$. From isobutyl-oxanthranol, HI, and P (L.). Oil; oxidised by CrO_3 in HOAc to isobutyl-oxanthranol and finally to anthraquinone.

BUTYL-ANTHRANOL-DIHYDRIDE

$C_6H_4<\begin{matrix}CH(OH)\\CH(C_4H_9)\end{matrix}>C_6H_4$. [72°]. From anthraquinone, aqueous NaOH and zinc-dust, boiled for some time and then iso-butyl bromide added (Liebermann, *A.* 212, 103).

ISO-BUTYL-ANTHRANYL CHLORIDE

$C_6H_4<\begin{matrix}CCl(C_4H_9)\\CO\end{matrix}>C_6H_4$. [78°]. Tables. Prepared by the action of PCl_5 on isobutyl-oxanthranol (Liebermann a. Walder, *B.* 14, 463).

n-BUTYL-BENZENE $C_{10}H_{14}$ *i.e.* $C_6H_5.CH_2Pr$. *Phenyl-butane.* (180°). S.G. $\frac{15}{}$ ·862. From *n*-propyl bromide, benzyl chloride, and Na (Radziszewski, *B.* 9, 260). Also from *n*-butyl bromide, bromo-benzene, and Na (Balbiano, *B.* 10, 296).

Bromination.—By the action of bromine in the dark, or in presence of iodine, the product is probably a mixture of *o*- and *p*- bromo-butyl-benzene. By the action of bromine in direct sunshine, the substitution takes place in the γ-position of the side-chain giving $C_6H_5.CHBr.C_3H_7$ or $C_6H_5.CBr_2.C_3H_7$. If the γ-mono-bromo-derivative is further brominated in the dark at 100° the second Br atom probably enters the β- position, the product being identical with the butylene-benzene-dibromide [70°] of Radziszewski (Schramm, *B.* 18, 1275).

ISO-BUTYL-BENZENE $C_6H_5.CH_2Pr$. (167°). S.G. ^{2} ·880 (G.); ·858 (R.). V.D. 4·72 (G.).

Formation.—1. From isobutyl bromide, bromo-benzene and Na (Riess, *B.* 3, 779; Wreden a. Znatowicz, *B.* 9, 1606).—2. From benzyl chloride, isopropyl iodide, and Na (Köhler a. Aronheim, *B.* 8, 509).—3. By the action of 50 g. iso-butyl chloride on 150 g. benzene in presence of about 5[illegible] g. Al_2Cl_6 (Gossin, *Bl.* [2] 41, 446).—4. By heating benzene with isobutyl alcohol and $ZnCl_2$ (Goldschmidt, *B.* 15, 1066). 5. By distilling *m*- or *p*- isobutyl-benzoic acid with lime (Kelbe a. Pfeiffer, *B.* 19, 1728).

Properties.—Colourless liquid; CrO_3 oxidises it to benzoic acid. Passed over red-hot PbO it forms naphthalene.

Sec-butyl-benzene $CH_3.CH_2.CH(C_6H_5).CH_3$. (171°). S.G. ^{19} ·873. From $C_6H_5.CHBr.CH_3$ and $ZnEt_2$ (Radziszewsky, *B.* 9, 261).

(α)-n-BUTYL-BENZENE SULPHONIC ACID $C_6H_4(CH_2Pr)SO_3H$. Formed by sulphonating *n*-butyl-benzene (Balbiano, *G.* 7, 343).—BaA'_2: small laminæ, sl. sol. cold water.—$ZnA'_2$7aq.—PbA'_2aq.—$MnA'_2$6aq.

(β)-*n*-Butyl-benzene sulphonic acid. Formed at the same time as the preceding (B.).—$BaA'_2$2aq: nodules, more soluble than the Ba salt of the (α)-acid.—$PbA'_2$2aq.

Iso-Butyl-benzene-sulphonic acid $C_6H_4(C_4H_9).SO_3H$. Formed by sulphonation of isobutyl-benzene.—A'_2Ba2aq: glistening plates.—A'K aq: plates.

Amide $C_6H_4(C_4H_9).SO_2NH_2$: [137°]; glistening needles (Kelbe a. Pfeiffer, *B.* 19, 1728).

BUTYL BENZOATE *v.* p. 470.

BUTYL BENZIMIDO-ETHER *v.* p. 479.

m-ISO-BUTYL-BENZOIC ACID

$C_6H_4(C_4H_9)CO_2H$ [1:3]. [127°]. Long stout needles. Formed by oxidation of *m*-isobutyl-toluene with dilute HNO_3. By further oxidation with dilute HNO_3 at 170°-200° isophthalic acid is formed. Gives a nitro- derivative [140°].—AgA': white pp.

Amide $C_6H_4(C_4H_9).CONH_2$: [130°]; hair-fine needles from water (Kelbe a. Pfeiffer, *B.* 19, 1725).

p-Isobutyl-benzoic acid $C_6H_4(C_4H_9).CO_2H$ [1:4]. [164°].

Formation.—1. By oxidation of *p*-isobutyl-toluene with dilute HNO_3. By further oxidation with dilute HNO_3 terephthalic acid is formed (Kelbe a. Pfeiffer, *B.* 19, 1725).—2. By saponification of its nitrile (Pahl, *B.* 17, 1237).

Properties.—Monoclinic crystals; gives a nitro- derivative [16[illegible]°].

Salts. — AgA': white flocculent pp.—BaA'_2xaq: plates, sol. hot water.—CaA'_2xaq: sl. sol. cold water.

Amide $C_6H_4(C_4H_9).CONH_2$: [171°]; long hair-fine needles (from water).

Methyl ether MeA': (247°); oil.

Nitrile $C_6H_4(C_4H_9).CN$. (249°) (G. a. M.); (244°) (K.); (238°) (P.). V.D. 5·47 (obs.) (K.); 5·35 (obs.) (P.). Colourless oil. *Formation.*—1. By distilling the formyl derivative of isobutyl-phenyl-amine with zinc-dust; the yield is about 12 p.c. (Gasiorowski a. Merz, *B.* 18, 1009).—2. By heating *p*-isobutyl-phenyl-thio-carbimide with copper powder at 200° (Pahl, *B.* 17, 1236). 3. Formed by heating tri-isobutylphenyl-phosphate with dry KCN (Kreysler, *B.* 18, 1707).

ISO-BUTYL-BENZOYL-ACETIC ETHER *v.* p. 482.

ISO-BUTYL BORATE $B(OC_4H_9)_3$. (212°). Formed by heating B_2O_3 with isobutyl alcohol for 8 hours at 170°. Burns with green flame. Insol. water and slowly decomposed by it (Councler, *J. pr.* [2] 18, 382). Not acted upon by ammonia.

***n*-BUTYL BROMIDE** C_4H_9Br *i.e.* $CH_3.CH_2.CH_2.CH_2Br$. (101° cor.). S.G. $\frac{0}{}$ 1·305; $\frac{20}{}$ 1·299. From *n*-butyl alcohol, Br, and P (Lieben a. Rossi, *A.* 158, 161). With Br at 150° it gives $C_4H_8Br_2$ (166°) (Linnemann, *A.* 161, 199). With bromine containing iodine at 250° it reacts thus: $C_4H_9Br + 8Br_2 = 2C_2Br_4 + 9HBr$ (Merz a. Weith, *B.* 11, 2244).

Isobutyl bromide $Pr.CH_2.Br$. (92°) (L.); (91°) at 758 mm. (Schiff, *B.* 19, 563). S.G. $\frac{15}{15}$ 1·2722; $\frac{25}{25}$ 1·2598 (Perkin, *C. J.* 45, 457). S.V. 110·39. M.M. 8·003 at 16° (P.). From the alcohol and HI or P and I (Pierre a. Puchot, *J. Ph.* [4] 13, 9; Wurtz, *A.* 93, 114; Chapman a. Smith, *C. J.* 22, 153). At 220° it partially changes to tertiary butyl bromide (Eltekoff, *B.* 8, 1244).

Tertiary butyl bromide CMe_3Br. (72°). S.G. $\frac{20}{}$ 1·215; $\frac{15}{15}$ 1·2020; $\frac{25}{25}$ 1·1892. V.D. 4·7 (obs.). M.M. 8·238 at 18°. From isobutylene and HBr (Roozeboom, *B.* 14, 2396). From tri-methyl carbinol and PBr_3 (Reboul, *C. R.* 93, 69).

Reactions.—1. Readily decomposes into HBr and isobutylene. This occurs when it is treated with Ag_2O, with KHO, with NEt_3, or with Zn and water (Butlerow, *Z.* 1867, 362).—2. With ZnO it forms tri-isobutylene, $C_{12}H_{24}$.—3. With *water*, even in the cold, it forms tertiary butyl alcohol.

BUTYL BUTYRATE *v.* Butyric acid.

ISO-BUTYL CARBAMINE C_4H_9NC. (c. 116°). S.G. $\frac{4}{}$ ·787. Preparation and properties like those of ethyl carbamine. Less readily attacked by HCl than ethyl carbamine (Gautier, *A.* 152, 221; *Bl.* [2] 11, 211; *Z.* [2] 5, 445).

***n*-BUTYL CARBONATE** $(PrCH_2)_2CO_3$. (207° cor.) at 740 mm. S.G. $\frac{0}{}$ ·941 (Lieben a. Rossi, *A.* 165, 112).

Isobutyl carbonate $(Pr.CH_2)_2CO_3$. (190° cor.). S.G. $\frac{15}{}$ ·919. From isobutyl iodide and Ag_2CO_3 (De Clermont, *A. Ch.* [3] 44, 336). From isobutyl alcohol and CyCl (Humann, *A. Ch.* [3] 44, 340). From sodium isobutylate and chloropicrin (Rœse, *A.* 205, 253; *cf.* Wurtz, *A.* 93, 119).

Isobutyl-orthocarbonate $(PrCH_2O)_4C$. (245° cor.). S.G. $\frac{8}{}$ ·900. The chief product of the action of chloropicrin on sodium isobutylate (Rœse, *A.* 205, 253).

BUTYL-CHLORAL *v.* Tri-chloro-butyric aldehyde.

***n*-BUTYL CHLORIDE** C_4H_9Cl *i.e.* $CH_3.CH_2.CH_2.CH_2Cl$. Mol. w. 92·5. (78° cor.). S.G. $\frac{0}{}$ ·907; $\frac{14}{}$ ·897 (Linnemann, *A.* 161, 197). S.V. 114·3 (Ramsay). From *n*-butyl alcohol and HCl (L.; *cf.* Lieben a. Rossi, *A.* 158, 161). From *n*-butane and chlorine (Schöyen, *A.* 130, 235).

Isobutyl chloride $(CH_3)_2CH.CH_2Cl$. (69°). S.G. $\frac{15}{}$ ·880 (Linnemann); $\frac{15}{15}$ ·8836; $\frac{25}{25}$ ·8739 (Perkin, *C. J.* 45, 455). M.M. 6·144 at 21°. H.F. p. 45,370. H.F. v. 43,050 (*Th.*). S.V. 114·26 (R. Schiff, *B.* 19, 562). From isobutyl alcohol and HCl or PCl_5 (Wurtz, *A.* 93, 113; Pierre a. Puchot, *C. R.* 72, 832).

Tertiary butyl chloride $(CH_3)_3C.Cl$. (51°). S.G. $\frac{15}{15}$ ·8471; $\frac{25}{25}$ ·8368. M.M. 6·257 at 15°.

Formation.—1. By action of chlorine on $(CH_3)_3CH$ (Butlerow, *J.* 1864, 497).—2. By heating isobutylene, $(CH_3)_2C:CH_2$, with conc. HCl at 100° (Saleskky, *A.* 165, 92; *B.* 5, 480; Le Bel, *Bl.* [2] 28, 462; Puchot, *A. Ch.* [5] 28, 549).—3. From tri-methyl-carbinol and AcCl or PCl_5.—4. From isobutyl iodide and ICl (Linnemann, *A.* 162, 18).

Properties.—With water (5 vols.) at 100° it is readily converted into tertiary butyl alcohol (Butlerow, *A.* 144, 33). It partakes, therefore, somewhat of the character of an acid chloride.

BUTYL-CHLORO- *v.* Chloro-butyl-.

BUTYL-CINCHONIC ACID *v.* Butyl-quinoline-carboxylic acid.

BUTYL-CRESOL *v.* Methyl-butyl-phenol.

ISO-BUTYL CYANATE $Pr.CH_2.N.CO$. (110°). From isobutyl iodide and silver cyanate (Brauner, *B.* 12, 1877).

Tertiary butyl cyanate $(CH_3)_3C.N.CO$. (86° cor.). S.G. $\frac{0}{}$ ·8676. The chief product of the action of isobutyl iodide on silver cyanate (B.)

BUTYL CYANIDE *v.* Valeronitrile.

***n*-BUTYLENE** C_4H_8 *i.e.* $CH_3.CH_2.CH:CH_2$. *Vinyl-ethane. Ethyl-ethylene.* Mol. w. 56. (c. −4°). Occurs in the oils deposited from compressed coal-gas (Colson, *Bl.* [2] 48, 52; *C. R.* 104, 1286).

Formation.—1. By boiling *n*-butyl iodide with alcoholic KOH (Grabowsky a. Saytzeff, *A.* 179, 325; Lieben a. Rossi, *A.* 158, 164).—2. From bromo-ethylene and $ZnEt_2$ (Chapman, *C. J.* 20, 28; Wurtz, *Z.* [2] 5, 407).—3. Together with secondary butyl alcohol by the action of HNO_2 on *n*-butyl-amine (Meyer, *B.* 10, 136).

Properties.—Gas. Forms with Br a dibromide (167°). HI forms $CH_3.CH_2.CHI.CH_3$.

ψ-Butylene $CH_3.CH:CH.CH_3$. *(β)-Butylene. s-Di-methyl-ethylene.* (1°).

Occurrence.—In the oils from compressed coal-gas (Colson, *C. R.* 104, 1286).

Formation.—1. From secondary butyl iodide and alcoholic KOH, Ag_2O and water, or AgOAc (De Luynes, *A.* 129, 200; 132, 275; Lieben, *A.* 150, 108; 151, 121).—2. Together with isobutylene by distilling *n*- or *iso*- butyl alcohol with $ZnCl_2$ (Nevolé, *Bl.* 24, 122; Le Bel a. Greene, *Am.* 2, 23; *Bl.* [2] 29, 306).—3. By heating secondary butyl alcohol.—4. From MeI, allyl iodide, and Na, small quantities of the two other butylenes being also formed (Wurtz, *Bl.* [2] 8, 265; Grosheintz, *Bl.* [2] 29, 201).—5. H_2SO_4 acting on isobutyl alcohol forms (1 vol. of) $CH_3.CH:CH.CH_3$ and (2 vols. of) $(CH_3)_2C:CH_2$ (Konovaloff, *Bl.* [2] 34, 333; *cf.* Puchot, *A. Ch.* [5] 28, 508).—6. By boiling isobutyl iodide with PbO (Eltekoff, *Bl.* [2] 34, 347).

Properties.—Gas. Br gives $C_4H_8Br_2$ (156°–159°). HI gives $CH_3.CH_2.CHI.CH_3$.

Isobutylene $(CH_3)_2C:CH_2$. *u-Di-methyl-ethylene.* (−6°). S.G. $\frac{-14}{4}$ ·637 (Puchot). H.F. p. 10,660. H.F.v. 8920 (*Th.*). V.D. 1·93 (calc. 1·94). Occurs in the oils obtained by compressing oil-gas (Faraday, *T.* 1825, 440) or coal-gas (Colson, *Bl.* [2] 48, 52; *cf.* Prunier, *Bl.* [2] 19, 109).

Formation.—1. By electrolysis of potassium

valerate (Kolbe, *A.* 69, 269).—2. From *sec-* or *tert-* butyl alcohol and H_2SO_4 or $ZnCl_2$ (Wurtz, *A.* 93, 107; Konovaloff, *Bl.* [2] 34, 333; Lermontoff, *A.* 196, 117; Puchot, *A. Ch.* [5] 28, 508; *C. R.* 85, 757; Scheschukoff, *Bl.* [2] 45, 181; *cf.* Nevolé, *Bl.* [2] 24, 122).—3. Together with ethylene and propylene by passing fusel oil through a red-hot tube (Wurtz, *A.* 104, 249; Butlerow, *A.* 145, 277).—4. From *iso-* or *tert-* butyl iodide and alcoholic KOH (De Luynes, *C. R.* 56, 1175; *A. Ch.* [4] 2, 385; Butlerow, *A.* 144, 19; *Z.* [2] 6, 236).—5. By heating di-methyl-acrylic acid to 210°-220° during 25-30 hours (Gorboff a. Kessler, *Bl.* [2] 41, 392).

Preparation.—Isobutyl iodide is run into boiling alcoholic KOH and the gas collected.

Properties.—Gas, sl. sol. water, v. sol. alcohol, v. e. sol. ether and HOAc.

Reactions.—1. Conc. HCl at 100° forms *tert*-butyl chloride.—2. Conc. HI aq absorbs it, forming tert-butyl iodide and tri-methyl carbinol (Scheschukoff, *Bl.* [2] 46, 823).—3. Conc. H_2SO_4 (3 pts.) mixed with water (1 part) absorbs it, and on diluting with water and distilling *tert*-butyl alcohol is got. H_2SO_4 (5 pts.) mixed with less water (1 pt.) forms much dodecylene.—4. Br in CS_2 forms $C_4H_8Br_2$ (148°) and $C_4H_7Br_3$ (173°-183°) at 235 mm. (Nevolé, *C. R.* 83, 65; Norton a. Williams, *Am.* 9, 88).—5. HClO forms a chloro-butyl alcohol (137°) (Butlerow, *A.* 144, 1; *Z.* [2] 6, 236; Henry, *Bl.* [2] 26, 23).—6. CrO_3 gives acetone, oxalic acid, acetic acid, &c. (Zeidler, *A.* 197, 251).—7. Cl forms isobutenyl chlorides C_4H_7Cl (Scheschukoff, *J. R.* 16, 488).

Combinations.—$(C_4H_8)_2Al_2Cl_6$. From ethylene, Al_2Cl_6, and HCl (Gustavson, *J. R.* 16, 97).—$(C_4H_8)_2Al_2Br_6$: oil. S.G. $\frac{0}{}$ 2·1. *V.* p. 147.

BUTYLENE ALCOHOL *v.* Di-oxy-butane.

BUTYLENE DIAMINE $C_4H_{12}N_2$ *i.e.* $C_4H_8(NH_2)_2$ (?). (above 140°). From ethylene cyanide, tin, and HCl (Fairley, *C. J.* 17, 362; could not be obtained by Ladenburg, *B.* 16, 1150, or Lellmann a. Würthner, *A.* 228, 22?).—$B'_2H_2PtCl_6$.

BUTYLENE BROMIDE *v.* Di-bromo-butane.

BUTYLENE TRI-CARBOXYLIC ACID $CH_3.CH:C(CO_2H).CH(CO_2H)_2$. *Ethylidene-ethenyl-tri-carboxylic acid.* [185°]. Formed by the action of *a*-chloro-crotonic ether upon sodio-malonic ether, and saponification of the product (Hjelt, *B.* 17, 2833). V. sol. water, m. sol. ether.—$A'''Ag_3$: flocculent pp.—A'''_2Ca_3× and A'''_2Ba_3×: easily soluble powders.

Mono-ethyl ether $A'''H_2Et$ 3aq: [70°]: large triclinic crystals, $a:b:c = \cdot9111:1:\cdot7553$.—$A'''H_2Et$ aq [145°].

Tri-ethyl ether Et_3A'''. (286°).

BUTYLENE GLYCOL *v.* Di-oxy-butane.

BUTYLENE GLYCOL CHLORHYDRIN *v.* Chloro-butyl alcohol.

BUTYLENE CYANAMINE $C_6H_{13}N_5$. [173°]. Formed by heating guanidine isovalerate at 225°. Trimetric needles, m. sol. cold water. Converted by conc. H_2SO_4 into butylene guanamide $C_6H_{11}N_3O_2$, whence HNO_3 forms cyanuric acid (Bandrowski, *B.* 9, 240).—B'HCl.—$B'AgNO_3$.—$B'_2H_2SO_4$.

BUTYLENE HYDRATE *v.* *Sec*-Butyl alcohol.

BUTYLENE NITRITE (?) $C_4H_8N_2O_4$. From isobutylene and conc. HNO_3 (Haitinger, *M.* 2, 287).

Butylene nitrite (?) [96°]. Formed by boiling petroleum of Tiflis with HNO_3 (Beilstein a. Kurbatoff, *B.* 14, 1621).

ISO-BUTYLENE OXIDE C_4H_8O *i.e.* $O<\begin{smallmatrix}CMe_2\\CH_2\end{smallmatrix}>$. (52°). S.G. $\frac{0}{}$ ·8311. From isobutylene with successive treatment with HClO and KOH (Eltekoff, *Bl.* [2] 10, 23; *J. R.* 1?, 368). Water, at ordinary temperatures, unites with it, forming di-oxy-butane.

s-**Butylene oxide** $O<\begin{smallmatrix}CHMe\\CHMe\end{smallmatrix}>$. (57°). S.G. $\frac{0}{}$ ·8344. Formed similarly from $CH_3.CH:CH.CH_3$ (E.). Water at 100° forms di-oxy-butane $CH_3.CH(OH).CH(OH).CH_3$.

BUTYL ENNYL KETONE $C_{14}H_{28}O$ (?) or $C_4H_9.CO.C_4H_8(C_5H_{11})$. *Amyl valerone.* (209°). S.G. $\frac{12}{}$ ·845. From CO on sodium amylate, $NaOC_5H_{11}$, at 160° (Geuther a. Fröhlich, *A.* 202, 301). Liquid, does not combine with $NaHSO_3$.

BUTYL ETHER *v.* Butyl oxide.

BUTYL-FORMIC ACID *v.* Valeric acid.

BUTYL-GLYCERIC ACID *v.* Di-oxy-butyric acid.

BUTYL-GLYCIDIC ACID *v.* Di-oxy-butyric acid.

BUTYL GLYCOL *v.* Di-oxy-butane.

BUTYL-GLYOXALINE $C_3H_3(C_4H_9)N_2$. *Glyoxal-amyline.* [121°]. (274°). Flat needles. Sl. sol. water. Prepared by the action of valeric aldehyde-ammonia on glyoxal (Radziszewski, *B.* 16, 747; 17, 1291). Br forms $C_7H_{10}Br_2N_2$ [158°] and $C_7H_9Br_3N_2$ [217°].

Salts.—B'HCl [136°].—B'HBr [100°].—$B'H_2C_2O_4$ [196°].—$B'_2H_2PtCl_6$.

ISO-BUTYL DIGUANIDE $C_6H_{15}N_5$ *i.e.* $C_2H_6N_5(C_4H_9)$. The sulphate of the copper derivative $Cu(C_6H_{14}N_5)_2H_2SO_4$ is formed by the action of aqueous $CuSO_4$ and isobutylamine on dicyandiamide at 100° (Smolka, *M.* 4, 815). Alkaline syrup, absorbing CO_2 from the air.

Salts.—$B'_2H_2SO_4$ 1½aq. S. 26·3 at 16°. Colourless transparent leaflets.—$B'H_2SO_4$ 1½aq.—B'HCl. [216°]. S. 40 at 16°.—B'2HCl. [194°]. Deliquescent.—$B'_2H_2PtCl_6$ aq: golden four-sided tables.—$B'_2H_2CrO_4$ aq.—$B'_2H_2C_2O_4$.

Metallic derivatives $Cu(C_6H_{14}N_5)_2$: silky red needles, sl. sol. water, sol. dilute acids.—$Cu(C_6H_{14}N_5)_2 2HNO_3$.—$Cu(C_6H_{14}N_5)_2H_2Cl_2$ aq.—$Cu(C_6H_{14}N_5)_2H_2SO_4$: carmine-red grains. S. ·26 at 18°.—$Cu(C_6H_{14}N_5)_2H_2SO_4$ aq: pale red grains.—$Cu(C_6H_{14}N_5)_2H_2SO_4$ 3aq: light rose-red crystals.

n-**BUTYL HEPTYL-OXIDE** $C_4H_9.O.C_7H_{15}$. (205·7°). S.G. $\frac{0}{0}$ ·8023. S.V. 271·3. C.E. (0°-10°) ·00097 (Dobriner, *A.* 243, 8).

BUTYL-HYDRO-ANTHRANOL *v.* Butyl-anthranol dihydride.

ISO-BUTYL HYPOPHOSPHATE $(C_4H_9)_4P_2O_6$. S.G. $\frac{15}{}$ 1·125. From isobutyl iodide and $Ag_4P_2O_6$ at 140° (Sänger, *A.* 232, 12). Oil. Decomposed by hot water.

Iso-butyl-hypophosphate of barium $(C_4H_9)BaHP_2O_6$ 5aq. Needles.

BUTYLIDENE-ACETO-ACETIC ETHER *v.* p. 24.

ISO-BUTYLIDENE-AMIDO-BENZOIC ACID $C_{11}H_{13}NO_2$ *i.e.* $Pr.CH:N.C_6H_4CO_2H$. [145°-150°]. From amido-benzoic acid and iso-butyric aldehyde (Schiff, *A.* 210, 114). Slender needles, decomposed by cold dilute alkalis.

TRI-ISO-BUTYLIDENE DI-AMINE v. *Hydrobutyramide* under ISOBUTYRIC ALDEHYDE.

ISO-BUTYLIDENE CHLORIDE v. DI-CHLORO-ISOBUTANE.

ISO-BUTYLIDENE-ETHYLENE-ANILINE v. DI-PHENYL-ISOPROPYL-METAPYRAZOL TETRAHYDRIDE.

***n*-BUTYL IODIDES** $CH_3.CH_2.CH_2.CH_2.I$. Mol. w. 184. (131° cor.). S.G. $\frac{20}{4}$ 1·617 (Brühl); $\frac{0}{0}$ 1·6476. S.V. 128·2. C.E. (0°-10°) ·00098 (Dobriner, *A.* 243, 30). μ_β 1·510. R_∞ 54·47. From *n*-butyl alcohol and HI (Linnemann, *A.* 161, 196). ICl_3 at 250° acts on it thus: $C_4H_9I + 11ICl_3 = 2C_2Cl_6 + 9HCl + 12ICl$ (Krafft, *B.* 10, 805).

Secondary *n*-butyl iodide $CH_3.CH_2.CHI.CH_3$. (118°). S.G. $\frac{0}{0}$ 1·626; $\frac{20}{0}$ 1·592; $\frac{30}{0}$ 1·579 (Lieben); ^{0} 1·632; ^{20} 1·600 (Luynes). V.D. 6·6 at 20° (obs.). *Formation.*—1. By distilling erythrite with HI (De Luynes, *A.* 125, 252; *Bl.* 2, 3).—2. From ethyl-chloro-ethylic ether $CH_2Cl.CEtH.O.Et$ and HI at 140° (Lieben, *A.* 150, 87).—3. From *n*-butylene and HI (Wurtz, *A.* 152, 23).

Isobutyl iodide $(CH_3)_2CH.CH_2I$. (120°). S.G. $\frac{20}{4}$ 1·606 (Brühl); $\frac{15}{15}$ 1·6139, $\frac{25}{25}$ 1·6007 (Perkin, *C. J.* 45, 462). μ_β 1·506. R_∞ 54·41. S.V. 128·28 (Schiff, *B.* 19, 564). C.E. (0°-20°) ·0110 (Brauner, *A.* 192, 69). M.M. 12·199 at 19·4°. From isobutyl alcohol and HI. Distils constantly with 21 pts. water at 96° (Pierre a. Puchot, *C. R.* 74, 224). Treated with AgNCS gives a product, $(CH_3)_2CH.CH_2NCS$, which on saponification yields isobutylamine and, in greater quantity, tertiary butylamine (B.). Heated with lead oxide it yields pseudo-butylene besides iso-butylene (Eltekoff, *Bl.* [2] 34, 347).

Tertiary butyl iodide Me_3CI. (100°). S.G. ^{0} 1·571. *Formation.*—From tertiary butyl alcohol and HI.

Preparation.—By passing isobutylene (*q. v.*) into fuming HI, cooled with ice and well shaken (Markownikoff, *Z.* [2] 6, 29).

Reactions.—1. If the iodide (20 g.) be shaken with water (30 g.) for two days it dissolves, being converted into the alcohol: $Me_3CI + H_2O = Me_3C.OH + HI$ (Dobbin, *C. J.* 37, 237).—2. With dry ZnO it forms tri-isobutylene.—3. With sodium it forms isobutylene, tri-isobutylene, and hydrogen, with small quantities of a hydrocarbon not absorbable by H_2SO_4 (Dobbin).—4. Moist Ag_2O, Zn and water, and AgOAc, form isobutylene (Butlerow, *Z.* [2] 6, 237).—5. With MeOH at 100°-110° it gives MeI and trimethyl carbinol (Bauer, *A.* 220, 163).—6. With MeOAc at 110° it forms isobutylene, HOAc and MeI.

DI-BUTYL-KETINE v. DI-METHYL-DI-BUTYL-PYRAZINE.

DI-ISOBUTYL KETONE $C_9H_{18}O$ *i.e.* $C_4H_9.CO.C_4H_9$. *Valerone.* Mol. w. 142. (182°). S.G. ^{20} ·833. Formed, in small quantity, by distilling calcium valerate (6 pts.) with CaO (1 pt.) (Löwig, *P.* 42, 412; Ebersbach, *A.* 106, 268; Schmidt, *B.* 5, 600). Does not combine with $NaHSO_3$.

DI-ISOBUTYL-KETONE-SULPHONIC ACID $C_4H_8(HSO_3)—CO—C_4H_8(HSO_3)$. The sodium salt is formed by leaving phorone in contact with a saturated solution of $NaHSO_3$ for 2 or 3 weeks. It forms colourless prisms ($A''Na_2 2\frac{1}{2}aq$): soluble in water and alcohol (Pinner, *B.* 15, 593).

BUTYLLACTIC ACID v. OXY-BUTYRIC ACID.

BUTYL-LUTIDINE v. DI-METHYL-BUTYL-PYRIDINE.

***n*-BUTYL-MALONIC ACID** $C_7H_{12}O_4$ *i.e.* $C_4H_9.CH(CO_2H)_2$. [101°]. Prepared by saponification of the nitrile $C_4H_9.CH(CN).CO_2Et$ obtained by the action of KCN on chloro-hexoic-ether. Thick prismatic crystals. V. sol. water, alcohol, and ether. It gives a reddish-violet colouration on warming with H_2SO_4. At about 150° CO_2 is evolved and it is converted into caproic acid.

Salts.—$A''Ba$: white plates. S. 2·98 at 24°.—$A''Pb$: very sparingly soluble white glistening plates. S. ·011 at 20°. $A''Cu aq$: blue glistening plates. S. ·086 at 22°.—$A''Ag_2$: white pp. S. ·119 at 23° (Hell a. Lumpp, *B.* 17, 2217).

Isobutyl-malonic acid $PrCH_2.CH(CO_2H)_2$. [107°]. From its ether (Hjelt, *J.* 1882, 875).

Ethyl ether Et_2A''. (225°). S.G. ^{17} ·983. From sodium malonic ether and isobutyl iodide.

***n*-BUTYL MERCAPTAN** C_4H_9SH. Mol. w. 90. (98°). S.G. $\frac{0}{0}$ ·858; $\frac{16}{0}$ ·843 (Saytzeff a. Grabowsky, *A.* 171, 251; 175, 351). HNO_3 gives butane sulphonic acid.

Isobutyl mercaptan (88°). S.G. ^{12} ·848 (Humann, *A.* 95, 256); ^{20} ·8357 (Nasini, *G.* 13, 301). V.D. 3·10 (obs.). R_∞ 27·47 (N.). Formed by distilling $K(C_4H_9)SO_4$ with aqueous KHS.—KSC_4H_9. — $Hg(C_4H_9S)_2$: pearly scales.—$Pb(C_4H_9S)_2$: yellow crystalline pp.

Secondary butyl mercaptan (85°). S.G. ^{17} ·830. From *sec*-butyl iodide and KHS.—$C_4H_9SAq.—(C_4H_9S)_2Hg$ [189°] (Reymann, *B.* 7, 1287).

TETRA-ISOBUTYL-METHYLENE-DI-AMINE $C_{17}H_{38}N_2$ *i.e.* $N(C_4H_9)_2.CH_2N(C_4H_9)_2$. (215°-255°). From 'trioxymethylene' (formic paraldehyde) and di-isobutylamine (Ehrenberg, *J. pr.* [2] 36, 117).—$B''H_2PtCl_6$ [198°]. Forms with CS_2 a compound $C_{17}H_{38}N_2CS_2$ [54°].

BUTYL-MUSTARD OIL v. BUTYL THIO-CARBIMIDE.

ISO-BUTYL-NAPHTHALENE $C_{14}H_{16}$ *i.e.* $C_{10}H_7(C_4H_9)$. (280°). Prepared together with (α-α) and (α-β)-dinaphthyl by heating naphthalene and isobutyl chloride in presence of aluminium chloride. Colourless oil, very slightly volatile in steam. Picric acid compound: [96°] aggregates of golden needles (Wegscheider, *M.* 5, 236).

ISO-BUTYL NITRATE $C_4H_9NO_3$. (123°). S.G. ^{0} 1·038. From $AgNO_3$, urea, and isobutyl iodide (Wurtz, *A.* 93 120; Chapman a. Smith, *Z.* 1869, 433).

ISO-BUTYL NITRITE $(CH_3)_2CH.CH_2O.NO$. (67°). S.G. ^{0} ·894. H.F.p. 47,800. H.F.v. 44,900 (*Th.*) (Chapman a. Smith, *Z.* 1869, 433; Pribram a. Handl, *M.* 2, 658; Bertoni a. Truffi, *G.* 14, 23).

Tertiary butyl nitrite $(CH_3)_3C.ONO$. (63°) (B.); (76°-78°) (T.). S.G. ^{0} ·8914 (B.). Formed together with a little of the isomeric nitrobutane (110°-130°) by distilling tertiary butyl iodide with silver nitrite (Tscherniak, *A.* 180, 155; *B.* 7, 962). Prepared by distilling tertiary butyl alcohol (1 mol.) with glyceryl tri-nitrite (1 mol.) (Bertoni, *G.* 15, 357).

BUTYL-PSEUDO-NITROLE v. NITROSO-NITRO-BUTANE.

BUTYL-NITROLIC ACID v. NITROSO-NITRO-BUTANE.

n-**BUTYL-OCTYL-OXIDE** $C_4H_9.O.C_8H_{17}$. (225·7°). S.G. $\frac{0}{0}$ ·8069. S.V. 295·7. C.E. (0°–10°) ·00097 (Dobriner, *A.* 243, 9).

ISO-BUTYL OXALATE v. OXALIC ACID.

ISO-BUTYL-OXAMIC ACID $PrCH_2.NH.CO.CO_2H$. From oxalic ether (1 mol.) and dry isobutylamine (1 mol.) at 160° (Malbot, *C. R.* 104, 229).—CaA'_2.

Di-isobutyl-oxamic acid $(PrCH_2)_2N.CO.CO_2H$. Similarly prepared from di-iso-butylamine (M.).

DI-ISO-BUTYL-OXAMIDE $(PrCH_2NH)_2C_2O_2$. [167°]. From oxalic ether (1 mol.) and iso-butylamine (2 mols.). Acute plates, insol. boiling water; may be sublimed (Malbot, *C. R.* 104, 228).

DI-BUTYL OXIDE $(C_4H_9)_2O$. Mol. w. 130. (141°). S.G. $\frac{0}{}$ ·784 (Lieben a. Rossi, *A.* 165, 110); $\frac{0}{0}$ ·7865. S.V. 197·3. C.E. (0°–10°) ·00109 (Dobriner, *A.* 243, 8).

Di-isobutyl oxide (100°–104°). From iso-butyl iodide and KOC_4H_9, or Ag_2O (Wurtz, *A.* 93, 117).

Di-sec-butyl oxide (121°). S.G. $\frac{21}{}$ ·756. From aldehyde hydrochloride and $ZnEt_2$ (Kessel, *A.* 175, 56; *B.* 7, 291).

p-**ISO - BUTYL - PHENOL** $C_4H_9.C_6H_4OH$. [99°]. (231°) (S.); (237°) (L.). 1. From amido-iso-butyl-benzene by the diazo- reaction (Studer, *A.* 211, 242; *B.* 14, 1474, 2187).—2. From phenol (100 g.), isobutyl alcohol (80 g.) and $ZnCl_2$ (240 g.) (Liebmann, *B.* 14, 1842; 15, 150, 1991; Dobrzycki, *J. pr.* [2] 36, 390). Needles (from alcohol). Volatile with steam. V. sol. alkalis. Gives a pp. with bromine-water, but no colour with Fe_2Cl_6. Is antiseptic. PCl_5 gives chloro-iso-butyl-benzene, which on oxidation gives p-chloro-benzoic acid. Gives a di-nitro- derivative [93°]. Fused with P_2O_5 it gives phenol and isobutylene. Ammonia and $ZnCl_2$ give $C_4H_9.C_6H_4NH_2$ (Lloyd, *B.* 20, 1254).

Methyl ether $C_4H_9.C_6H_4OMe$. (215·5°). S.G. $\frac{27}{}$ ·937.

Ethyl ether $C_4H_9.C_6H_4OEt$. (235°) (S.); (242°) (L.).

Benzoyl derivative $C_4H_9.C_6H_4OBz$. [83°] (S.); [80°] (Kreysler, *B.* 18, 1717); (335°); (344°) (K.). White plates (from alcohol).

Acetyl derivative $C_4H_9.C_6H_4OAc$. (245°). S.G. $\frac{24}{}$ ·999.

ISO-BUTYL-PHENOL SULPHONIC ACID $C_4H_9.C_6H_3(OH).SO_3H$. From isobutyl phenol and H_2SO_4 (Liebmann, *B.* 15, 1990).—BaA'_2 2aq.

ISO-BUTYL-PHENYL-AMINE v. AMIDO-PHENYL-BUTANE.

Di-isobutyl-di-phenyl-amine $(C_6H_4.C_4H_9)_2NH$. (290°–315°). Thick oil. Formed together with $C_6H_4(C_4H_9).NH_2$ by heating oxy-phenyl-isobutane $C_6H_4(C_4H_9).OH$ [1:4] with ammoniacal $ZnBr_2$ (or $ZnCl_2$) and NH_4Br (or NH_4Cl) at 320°–330°; the yield is 20–25 p.c.—$B'_2H_2Cl_2PtCl_4$: yellow needles.

Acetyl derivative $(C_6H_4.C_4H_9)_2NAc$: [75°]; glistening white plates; sl. sol. water, v. sol. alcohol and benzene (Lloyd, *B.* 20, 1255).

DI-ISO-BUTYL-DI-PHENYL CYANAMIDE $C_{21}H_{26}N_2$ *i.e.* $C(NC_6H_4.CH_2Pr)_2$. *Carbo-di-phen-isobutyl-imide.* [189°]. Formed by boiling a solution of di-isobutyl-di-phenyl-thio-urea in benzene with PbO (Pahl, *B.* 17, 1242). Colourless crystals. Sol. hot benzene, sl. sol. ether. By warm dilute alcohol it is converted into di-isobutyl-di-phenyl-urea. With amines it combines to form guanidines. Heated with CS_2 at 170° it yields isobutyl-phenyl-thio-carbimide.

ISO-BUTYL-PHENYLENE-DIAMINE $C_6H_4(NH_2)(NHCH_2Pr)$. [39°]. Formed by the reduction of p-nitroso-iso-butylaniline (Wacker, *A.* 243, 299). Plates (from ether); can be distilled. Its chloride forms white plates; v. sol. water, sl. sol. alcohol, insol. ether.

DI-p-ISO-BUTYL-DI-PHENYL-GUANIDINE $HN:C(NH.C_6H_4.C_4H_9)_2$. *Di-phenisobutyl-guanidine.* [173°]. Formed by heating an alcoholic solution of di-p-isobutyl-di-phenyl-thiourea with NH_3 and lead oxide (Pahl, *B.* 17, 1240). Colourless plates. V. sol. alcohol and benzene.—$B'_2H_2Cl_2PtCl_4$: yellow crystalline pp.

Tri-p-isobutyl-tri-phenyl-guanidine $C_4H_9.C_6H_4.N:C(NH.C_6H_4.C_4H_9)_2$. *Tri-phenisobutyl-guanidine.* [164°]. Obtained by digesting an alcoholic solution of di-p-isobutyl-di-phenyl-thiourea with p-isobutylphenyl-amine and lead oxide (P.). Small white needles. V. sol. benzene and hot alcohol.—$B'_2H_2Cl_2PtCl_4$: yellow needles.

ISO-BUTYL-PHENYL-(β)-NAPHTHYL-THIO-UREA $C_{10}H_7.NH.CS.NH.C_6H_4.C_4H_9$. *Phenisobutyl-($\beta$)-naphthyl-thiourea.* [152°]. Prepared by warming an alcoholic solution of (β)-naphthyl-thio-carbimide and isobutylphenyl-amine (Mainzer, *B.* 16, 2026). White plates. Sol. boiling alcohol. By phosphoric acid it is split up into isobutylphenyl - thio - carbimide, (β) - naphthyl - thio-carbimide, isobutylphenyl-amine, and (β)-naphthylamine.

ISO-BUTYLPHENYL-PHENYL-THIOUREA v. PHENYL-ISOBUTYLPHENYL THIOUREA.

TRI-ISO-BUTYLPHENYL-PHOSPHATE $PO(OC_6H_4.C_4H_9)_3$. (above 400°). Obtained by heating isobutyl-phenol with $POCl_3$; the yield is 90 p.c. of the theoretical (Kreysler, *B.* 18, 1700). Thick liquid. V. sol. ether, benzene, and warm alcohol, sl. sol. petroleum-ether.

TETRA-ISO-BUTYLPHENYL SILICATE $Si(OC_6H_4.C_4H_9)_4$. (c. 380°). Obtained by heating isobutyl-phenol with $SiCl_4$; the yield is 70 p.c. of the theoretical (Hertkorn, *B.* 18, 1692). Thick colourless oil. V. sol. benzene, chloroform, CS_2, etc.

p-**ISO-BUTYL-PHENYL-THIOCARBIMIDE** $SC:N.C_6H_4.(C_4H_9)$. *Phenisobutyl-mustard-oil.* [42°]. (277°). Formed by heating di-p-isobutyl-di-phenyl-thiourea with phosphoric acid (Pahl, *B.* 17, 1235). Long white needles. V. sol. alcohol and ether.

DI-p-ISO-BUTYL-DI-PHENYL-THIOUREA $SC(NH.C_6H_4.C_4H_9)_2$. *Di-phenisobutyl-thiourea.* [193°]. Formed by cohobating an alcoholic solution of p-isobutylphenyl-amine with CS_2 (Pahl, *B.* 17, 1235). Fine white needles. Sol. ether and benzene, sl. sol. alcohol, insol. water.

DI-p-ISO-BUTYL-DI-PHENYL-UREA $OC(NH.C_6H_4.C_4H_9)_2$. *Di - phenisobutyl - urea.* [284°].

Formation.—1. By the action of carbonyl chloride on p-isobutylphenyl-amine dissolved in benzene.—2. By cohobating an alcoholic solution of the thiourea with mercuric oxide (Pahl, *B.* 17, 1240). Colourless needles. Sol. hot alcohol, insol. water.

ISO-BUTYL-PHOSPHINE $C_4H_9PH_2$. (62°). Prepared, together with the following, from isobutyl iodide, ZnO, and PH_4I at 100° (Hofmann, *B.* 6, 296). Resembles ethyl-phosphine in preparation and properties.

Di-isobutyl phosphine $(C_4H_9)_2PH$. (153°).

Tri-isobutyl phosphine $(C_4H_9)_3P$. (215°). From the preceding and isobutyl iodide.

Tetra-isobutyl-phosphonium iodide $(C_4H_9)_4PI$. Crystalline.

ISO-BUTYL-PHOSPHINIC ACID $C_4H_9PO_3H_2$ [100°]. Paraffin-like solid (Hofmann, *B.* 6, 304). —A′Ag. Amorphous pp.

Di-isobutyl-phosphinic acid $(C_4H_9)_2PO_2H$. Oil.—A′Ag. Amorphous.

ISOBUTYL PHOSPHITE. *Dichloride.* $C_4H_9O.PCl_2$. (155°). S.G. $\frac{0}{}$ 1·191. A by-product in the conversion of isobutyl alcohol into isobutyl chloride by PCl_3 (Menschutkin, *A.* 139, 347).

DI-ISO-BUTYL-PINACONE $C_{14}H_{30}O_2$ *i.e.* $Pr.CH_2.CH_2.CMe(OH).CMe(OH).CH_2.CH_2.Pr$. *Di-oxy-tetra-decane. Tetra-decylene glycol.* [30°]. (268°). A product of the action of Na upon methyl iso-amyl ketone (Rohn, *A.* 190, 305: Purdie, *C. J.* 39, 468). Needles, insol. water.

BUTYL-METAPYRAZOLONE *v.* DI-OXY-BUTYL-METAPYRAZOL.

(*Py.* 3)-ISO-BUTYL-QUINOLINE $C_{13}H_{15}N$ *i.e.* $C_6H_4\left<\begin{matrix}CH{:}CH\\ |\\ N{=}C(C_4H_9)\end{matrix}\right.$ (271°). Colourless oily liquid. Formed by distilling its (*Py.* 1)-carboxylic acid with lime (Doebner, *B.* 20, 280; *A.* 242, 282).

Picric acid compound $B'.C_6H_3N_3O_7$. [161°]. Lemon-yellow plates (from alcohol).—$(B'HCl)_2PtCl_4$. Orange-red needles (from water).

(*Py.* 3)-ISO-BUTYL-QUINOLINE—(*Py.* 1)—CARBOXYLIC ACID

$C_{14}H_{15}NO_2$ *i.e.* $C_6H_4\left<\begin{matrix}C(CO_2H){:}CH\\ |\\ N{=\!=}C(C_4H_9)\end{matrix}\right.$. *Isobutyl-cinchonic acid.* [186°]. Formed by the action of isovaleric aldehyde upon pyruvic acid and aniline. White satiny plates (containing $1\frac{1}{2}$aq) (Doebner, *B.* 20, 279; *A.* 242, 280).—B′HClaq: plates.—$B'_2H_2PtCl_6$.—AgA′.

ISO-BUTYL SILICATE $(PrCH_2)_4SiO_4$. (c. 258°). S.G. $\frac{15}{}$ ·953. From $SiCl_4$ and isobutyl alcohol (Cahours, *C. R.* 77, 1408). Slowly decomposed by water.

BUTYL SULPHATES

***n*-Butyl-sulphuric acid** $Pr.CH_2.SO_4H$.

Salt.—BaA'_2aq: crystalline plates. S.G. $\frac{21}{}$ 1·778 (Lieben a. Rossi, *A.* 165, 116; Clarke, *B.* 11, 1506).

Isobutyl sulphuric acid $PrCH_2.SO_4H$. From the alcohol and H_2SO_4 (Wurtz, *C. R.* 35, 310).—KA′: laminæ (from alcohol).

Chloride $C_4H_9.O.SO_2Cl$. From isobutyl alcohol and SO_2Cl_2 (Behrend, *J. pr.* [2] 15, 34). Liquid.

***n*-BUTYL SULPHIDE** $(C_4H_9)_2S$. Mol. w. 146. (182°). S.G. $\frac{0}{0}$ ·852; $\frac{18}{0}$ ·839 (Saytzeff, *A.* 171, 253). From butyl iodide and K_2S.

Isobutyl sulphide $(Pr.CH_2)_2S$. (171° i. V.). S.G. $\frac{10}{}$ ·836. Formed by distilling isobutyl sulphate with conc. aqueous KHS (Beckmann, *J. pr.* [2] 17, 445).

Secondary butyl sulphide $(CMeEtH)_2S$ (165°). S.G. $\frac{23}{}$ ·832. Combines with MeI (Reymann, *B.* 7, 1288).

Isobutyl disulphide $(CH_2Pr)_2S_2$. (220°) (Spring a. Legros, *B.* 15, 1938).

ISO-BUTYL SULPHOCYANIDE $CH_2Pr.S.CN$. (175°) (Reimer, *B* 3, 757).

***n*-BUTYL SULPHONE** $(C_4H_9)_2SO_2$. [44°]. From fuming HNO_3 and $(C_4H_9)_2S$ (Grabowsky, *A.* 175, 348).

Di-isobutyl sulphone $(C_4H_9)_2SO_2$. [17°]. (265° i. V.). S.G. $\frac{18}{}$ 1·006. Di-isobutyl sulphoxide (100 pts.) is dissolved in water (1000 pts.) and oxidised by $KMnO_4$ (63 pts.) dissolved in water (1900 pts.). Excess of permanganate destroyed by sodic formiate and the sulphone extracted by ether. The yield is quantitative (Beckmann, *J. pr.* [2] 17, 448).

Properties.—White plates. Not affected by reducing agents

***n*-BUTYL SULPHOXIDE** $(C_4H_9)_2SO$. [32°]. From HNO_3 (S.G. 1·3) and $(C_4H_9)_2S$ (Grabowsky, *A.* 175, 348).

Di-isobutyl sulphoxide $(C_4H_9)_2SO$. [69°]. From di-isobutyl sulphide (1 pt.) and (2 pts. of) HNO_3 (S.G. 1·4) in the cold. Extracted with ether after neutralisation. The yield is quantitative (Beckmann, *J. pr.* [2] 17, 446).

Properties.—Yellow needles. Soluble in 2 parts of cold water, but separates as an oil on warming. Readily reduced to di-iso-butyl sulphide.

BUTYL SULPHURIC ACID *v.* BUTYL SULPHATE.

DI-ISO-BUTYL-THETINE $CO_2H.CH_2.S(C_4H_9)_2(OH)$. The hydrobromide is a syrup formed by the action of isobutyl sulphide on bromo-acetic acid at 100°. Lead converts it into crystalline $C_{10}H_{20}SO_2 5PbBr_2$ and $C_{10}H_{20}SO_2 3PbBr_2$ (Letts, *Pr. E.* 28, 588).

***n*-BUTYL THIO-CARBIMIDE** $CH_2Pr.N.CS$. Mol. w. 115. (167°). Formed by boiling *n*-butylamine with CS_2 and alcohol. Evaporating the alcohol and heating the residue with aqueous $HgCl_2$ (Hofmann, *B.* 7, 508). NH_3 gives butyl-thio-urea [79°].

Isobutyl thio-carbimide $CH_2Pr.N.CS$. (162°). S.G. $\frac{14}{}$ ·937. Similarly prepared. (H.). NH_3 gives isobutyl-thio-urea [94°].

Secondary isobutyl thio-carbimide CHMeEt.N.CS. (160°). S.G. $\frac{12}{}$ ·944. Similarly prepared. It is the essential constituent of the oil of scurvy-grass or spoon-wort (from *Cochlearia officinalis*) (Hofmann, *Z.* [2] 5, 400; *B.* 2, 102). NH_3 gives butyl-thio-urea [135°].

Tertiary butyl thio-carbimide $CMe_3.N.CS$. [11°]. (140°). S.G. $\frac{34}{}$ ·900 (Rudneff, *J. R.* 11, 179; *B.* 12, 1023).

BUTYL THIO-CARBONIC ACID *v.* THIO-CARBONIC ACID.

***n*-BUTYL-THIOPHENE** $C_4SH_3(C_4H_9)$ (181°). S.G. $\frac{12}{}$ ·957. Colourless oil. Formed by the action of sodium on a mixture of iodothiophene and butyl bromide (Meyer a. Kreis, *B.* 17, 1561).

BUTYL-THIO-UREAS. The preparation and properties of these bodies are analogous to those of the corresponding ethyl thio-ureas (*q. v.*).

***n*-Butyl thio-urea** $CH_2Pr.NH.CS.NH_2$. [79°]. From butyl thio-carbimide and NH_3 (Hofmann, *B.* 7, 512).

Isobutyl thio-urea [94°] (H.).

Sec-butyl thio-urea [133°] (H.).

Tert - **butyl thio - urea** $CMe_3.NH.CS.NH_2$. [165°] (Rudneff, *Bl.* [2] 33, 300). Prisms, sol. alcohol.

Di - *tert* - butyl thio - urea $SC(NHCMe_3)_2$. [162°]. From tert-butyl-amine, CS_2, and alcohol. Formed also by the action of tert-butyl thiocarbimide on tert-butyl-amine (Rudneff, *Bl.* [2] 33, 300).

***m*-ISO-BUTYL-TOLUENE** $C_6H_4(CH_3)(C_4H_9)$ [1:3]. (187°) (K. a. B.); (194°) (R.); (185°) (E.). *Methyl - isobutyl - benzene.* Colourless liquid. Occurs in oil of resin (Kelbe a. Baur, *B.* 16, 619, 2559; Renard, *A. Ch.* [6] 1, 250). Prepared by the action of isobutyl bromide on toluene in presence of Al_2Br_6 (K. a. B.). Formed by diazotising methyl - isobutyl - phenyl - amine and treating the diazo- salt with an excess of $SnCl_2$ (Effront, *B.* 17, 2329). On oxidation with HNO_3 it first gives *m*-iso-butyl-benzoic acid and finally isophthalic acid (Kelbe a. Pfeiffer, *B.* 19, 1723).

p-(*Iso*?) **-Butyl - toluene** $C_6H_4(CH_3)(C_4H_9)$ [1:4]. (178°). Occurs in oil of resin. HNO_3 oxidises it to *p*-toluic acid (Kelbe a. Baur, *B.* 16, 2562).

p-**Isobutyl-toluene** (c. 195°)? Formed by heating toluene with isobutyl alcohol and $ZnCl_2$ (Goldschmidt, *B.* 15, 1067). Formed, together with the *m*-isomeride, by the action of isobutyl bromide on toluene in presence of Al_2Br_6 (Kelbe a. Pfeiffer, *B.* 19, 1725). HNO_3 oxidises it to *p*-isobutyl-benzoic acid.

***m*-ISO-BUTYL-TOLUENE-SULPHONIC ACID** $C_6H_3(CH_3)(C_4H_9)(SO_3H)$ [1:3:*x*]. [76°]. Small hygroscopic plates. Formed by sulphonation of *m*-iso-butyl-toluene.

Salts.—KA′aq: large soluble pearly plates. —NaA′aq: needles. — $CuA'_2$4aq: large blue soluble plates.—BaA'_2aq: small plates, sl. sol. cold water and alcohol.—$PbA'_2$3aq: pearly plates.

Amide: [?5°], small plates, soluble in water (Kelbe a. Baur, *B.* 16, 2560).

p-(*Iso*?)-**Butyl-toluene-sulphonic acid** $C_6H_3(CH_3)(C_4H_9)(SO_3H)$ [1:4:*x*]. Obtained by sulphonation of *p*-isobutyl-toluene.

Salts. — KA′$1\frac{1}{2}$aq: small easily soluble plates.—NaA′2aq. — BaA'_2aq: small sparingly soluble plates.—CuA'_2xaq: easily soluble blue crystals. — $PbA'_2$3aq: small plates, sol. hot water.

Amide: [113°], large pearly plates, sl. sol. hot water (Kelbe a. Baur, *B.* 16, 2563).

ISO-BUTYL-*o*-TOLUIC ACID $C_6H_3(CH_3)(C_4H_9)CO_2H$ [1:3:6]. [140°]. Formed by saponification of its nitrile (Effront, *B.* 17, 2334). White needles. V. sol. alcohol and ether, sl. sol. hot water, insol. cold water.—**A′Ag**: colourless plates, v. sol. hot water.

Nitrile $C_6H_3(CH_3)(C_4H_9)CN$ [1:3:6]. [60°]. (248°). *Formation.*—1. By distilling the formyl derivative of methyl-isobutyl-phenyl-amine with zinc-dust.—2. By heating isobutyl-tolyl-thiocarbimide with copper powder (E.). Long white needles. V. sol. alcohol and ether, sl. sol. hot petroleum-ether, insol. water.

Iso-butyl-toluic acid $C_6H(CH_3)(C_4H_9)CO_2H$ [1:5:6]. [132°]. Formed by saponification of its nitrile (Effront, *B.* 17, 2343). White silvery plates. V. sol. alcohol and ether, sl. sol. hot water.—**A′Ag**: colourless plates, sol. hot water.

Nitrile $C_6H_3(CH_3)(C_4H_9)CN$ [1:5:6]. (243°). *Formation.* — 1. By distilling the formyl derivative of methyl-isobutyl-phenyl-amine with zinc-dust.—2. By heating isobutyl-tolyl-thiocarbimide with copper-powder (Effront, *B.* 17, 2343). Colourless oil, solidifies on freezing to a white crystalline mass. V. sol. alcohol and ether.

ISOBUTYL-TOLUIDINE *v.* METHYL-ISOBUTYL-PHENYL-AMINE.

BUTYL-TOLYL-AMINE *v.* METHYL-BUTYL-PHENYL-AMINE.

ISO-BUTYL-TOLYL-THIOCARBIMIDE $C_6H_3(CH_3)(C_4H_9)NCS$ [1:3:6]. [46°]. (275°-280°). Formed by the action of phosphoric acid on di-isobutyl-di-tolyl-thiourea (Effront, *B.* 17, 2336). Long white needles. V. sol. alcohol and ether.

Iso-butyl-tolyl-thio-carbimide $C_6H_3(CH_3)(C_4H_9)NCS$ [1:5:6]. [44°]. (267°). Formed by heating di-isobutyl-di-tolyl-thiourea with phosphonic acid (Effront, *B.* 17, 2345). White crystalline solid. V. sol. alcohol and ether.

DI-ISOBUTYL-DI-TOLYL-THIOUREA $SC(NH.C_6H_3(CH_3)(C_4H_9)[6:1:3])_2$ [184°]. Formed by digesting methyl-isobutyl-phenyl-amine with CS_2 in alcoholic solution (Effront, *B.* 17, 2335). Long thin silky needles. V. sol. ether, sl. sol. alcohol.

Di-isobutyl-di-tolyl-thiourea $SC(NH.C_6H_3(CH_3)(C_4H_9)[6:1:5])_2$. [175°]. White needles. Sol. hot alcohol. Formed by digesting methyl-isobutyl-phenyl-amine with an alcoholic solution of CS_2 (Effront, *B.* 17, 2344).

ISO-BUTYL-UREA. *Valeryl derivative* $NH(C_4H_9).CO.NH(CO.C_4H_9)$. [102°]. Flat needles. Sol. alcohol and ether, sl. sol. water. Formed by the action of KOH on a mixture of (2 mols. of) valeramide (isopropyl-acetamide) and (1 mol. of) bromine (Hofmann, *B.* 15, 758).

Iso-*tert*-di-butyl-urea $CMe_3.NH.CO.NH.CH_2Pr$. [163°]. From *tert*-butyl cyanate and isobutylamine (Brauner, *B.* 12, 1875).

Di-*tert*-butyl-urea $(CMe_3NH)_2CO$. [242°]. From *tert*-butyl cyanate and *tert*-butylamine (B.).

ISO-BUTYL-XANTHAMIDE *v.* THIO-CARBONIC ETHERS.

BUTYRAL *v.* BUTYRIC ALDEHYDE.

BUTYRAMIDE *v.* *Amide of* BUTYRIC ACID.

Di-isobutyramide $(C_3H_7.CO)_2NH$. [174°]. Formed by the action of ammonia on isobutyryl chloride (Hofmann, *B.* 15, 981). Long needles. Sublimable. Sol. alcohol. On distillation it splits up into isobutyric acid and isobutyronitrile.

***n*-BUTYRIC ACID** $C_4H_8O_2$ *i.e.* $CH_3.CH_2.CH_2.CO_2H$. Mol. w. 88. [c. −3°]. (162° cor.). S.G. $\frac{20}{4}$ ·9594 (Brühl); $\frac{0}{0}$ ·976 (Zander); $\frac{15}{15}$ ·9670; $\frac{25}{25}$ ·9588 (Perkin, *C. J.* 45). C.E. (0°–10°) ·00104 (Z.). M.M. 4·472 at 18·8° (P.). μ_β 1·4025. R_∞ 35·50. S.V. 107·85 (R. Schiff, *A.* 220, 105); 108·3 (Z.). S.H. ·440 at 0° (Schiff, *A.* 234, 300).

Occurrence.—1. Butter contains 2 p.c. of glyceryl butyrate (Chevreul, *A. Ch.* [2] 23, 23). Rancid butter contains free *n*-butyric acid (Grünzweig, *A.* 162, 193).—2. In crude wood vinegar.—3. In perspiration (Schotten, *J.* 1852, 704).—4. In muscular juice (Scherer, *A.* 69, 196).—5. In the contents of the large intestine.—6. As hexyl butyrate in oil got from fruit of *Heracleum*

giganteum.—7. The fruit of *Pastinaca sativa* contains octyl butyrate.—8. In cheese (*e.g.* of Limburg) (Iljenko, *A.* 63, 268).

A great many vegetable and animal juices and oils contain butyric acid, but in most cases it has not been determined whether the acid is *n-* or *iso-* butyric acid (Gorup-Besanez, *A.* 69, 369; Klinger, *A.* 106, 18; Krämer, *Ar. Ph.* [2] 54, 9; Wagner, *J. pr.* 46, 155; Scherer, *A.* 69, 196; Rebling, *Ar. Ph.* [2] 92, 83; 93, 300).

Formation.—1. A product of the fermentation of sugar, starch, milk, fibrin, and most kinds of vegetable and animal matter (Pelouze a. Gélis, *A. Ch.* [3] 10, 436; Lerch, *A.* 49, 215; Bonaparte, *C. R.* 21, 1070; Erdmann a. Marchand, *J. pr.* 29, 468; Wurtz, *A.* 52, 291; Scharling, *A.* 49, 313; Schubert, *J. pr.* 33, 256; Sullivan, *J.* 1858, 280; Ritthausen, *Z.* [2] 4, 314).—2. By fermentation of calcium lactate: $2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$. 3. Along with *n*-butyl alcohol by the fermentation of glycerin through a Schizomycetes in presence of $CaCO_3$ (Fitz, *B.* 9, 1348).—4. By the action of CrO_3 on albuminoids (Guckelberger, *A.* 64, 68).—5. By the action of HNO_3 on fats (Redtenbacher, *A.* 59, 49) and on Chinese wax (Buckton, *C. J.* 10, 166).—6. By oxidation of coniine (Blyth, *A.* 70, 89).—7. By the aceto-acetic ether synthesis (Frankland a. Duppa, *A.* 138, 218) *v.* ACETO-ACETIC ETHER.—8. By passing CO over a mixture of NaOEt and NaOAc at 200°: $C_2H_5NaO + C_2H_3NaO_2 + CO = CHNaO_2 + C_4H_7NaO_2$ (Fröhlich, *A.* 202, 306).

Preparation.—Sugar (6 kilos.), water (26 litres), and tartaric acid (30 g.) are left for some days, after which there is added putrid cheese (250 g.), sour skimmed milk (8 kilos.), and chalk (3 kilos.). The mixture is kept at 30° to 35° with occasional stirring. Calcium lactate is first formed, and this is afterwards decomposed with evolution of hydrogen (*v. Formation* 2); at the end of six weeks the evolution of gas ceases and the whole is now converted into calcic butyrate (Bensch, *A.* 61, 177, *cf.* Grillone, *A.* 165, 127; Lieben a. Rossi, *A.* 158, 146; and Fitz, *B.* 11, 52). Crude butyric acid may be purified by etherification, followed by saponification of the butyric ether (121°) (Bannoff, *B.* 19, 2552).

Properties.—Liquid, miscible with water, of powerful unpleasant smell. Separated from aqueous solution by $CaCl_2$. Its barium salt is more soluble in alcohol than those of formic, acetic, or propionic acids. Its calcium salt is ppd. by boiling a solution saturated in the cold.

Reactions.—1. Boiled with HNO_3 it gives succinic acid (Dessaignes; Erlenmeyer, *A.* 180, 207).—2. With CrO_3 it gives CO_2 and acetic acid (Grünzweig a. Hecht, *B.* 11, 1053).—3. With MnO_2 and dilute H_2SO_4 it gives propyl butyrate (Veiel, *A.* 148, 164).—4. The silver salt decomposes on dry distillation according to the equation:

$$4C_3H_7.CO_2Ag = 3C_3H_7.CO_2H + CO_2 + C + 4Ag$$

(Iwig a. Hecht, *B.* 19, 240).—5. Distillation over zinc-dust at 350° gives di-propyl ketone, propylene, CO, H, and other products (Jahn, *B.* 13, 2115).

Salts.—NaA′.—KA′. S. 125 at 15°. Very deliquescent.—MgA′ 5aq. Very soluble plates.—CaA'_2. S. 20 at 0°; 18 at 22°; 15 at 60°; 16·2 at 100° (Chancel a. Parmentier, *C. R.* 104, 474; Hecht, *A.* 213, 69). Trimetric needles.—CaA'_2 aq. S. 19·6 at 22°.—$(CaA'_2)_2(C_4H_8O_2)$ 5aq. $CaA'_2CaCl_2(C_4H_8O_2)_4$.—$CaCl_2(C_4H_8O_2)_2$ 2aq (Lieben, *M.* 1, 926).—SrA'_2. S. 40 at 22°.—BaA'_2 4aq. S. 40 at 14°. S. (alcohol) 11·7. Trimetric.—BaA'_2 2aq.—$BaA'_2C_4H_8O_2$ (Mixter, *Am.* 8, 343).—$BaA'_2 2CaA'_2$. Regular octahedra (Fitz, *B.* 13, 1314). ZnA'_2 2aq. S. 11 at 16°. Monoclinic prisms. Gives pp. of basic salt on boiling.—PbA'_2: oil.—PbA'_2 2PbO.—$PbA'_2 2CaA'_2$: cubes.—CuA'_2 2aq. Monoclinic.—CuA'_2 aq. Triclinic (Alth, *A.* 91, 176).—$CuA'_2 2Cu(AsO_2)_2$ (Wöhler, *A.* 94, 44).—AgA′. S. ·343 at 4·6°. Needles or monoclinic prisms.

Methyl ether (102°). S.G. $\frac{0}{0}$ ·9194 (Gartenmeister, *A.* 233, 249); $\frac{0}{4}$ ·9194 (Elsässer, *A.* 218, 314); ^{4} ·948 (Kahlbaum, *B.* 12, 344); $\frac{20}{4}$ ·8962 (Brühl); $\frac{15}{15}$ ·9037; $\frac{25}{25}$ ·8945 (Perkin, *C. J.* 45, 483). M.M. 5·387 at 16·4° (P.). S.V. 126·35 (R. Schiff, *A.* 220, 332). μ_β 1·3936 (Brühl). R_∞ 43·11 (B.). C.E. (0°-10°) ·001156 (E.).

Ethyl ether.—Mol. w. 116. (121° cor.). V.D. 3·99 (for 4·00) (S.). S.G. $\frac{0}{0}$ ·9004 (Gartenmeister); $\frac{0}{4}$ ·8996 (E.); ^{18} ·898 (Linnemann a. Zotta, *A.* 161, 178); $\frac{20}{4}$ ·8892 (B.); $\frac{15}{15}$ ·8849; $\frac{25}{25}$ ·8762 (P.). M.M. 6·477 at 16·1° (P.). S.V. 150·23 (S.). μ_β 1·4007. R_∞ 50·33 (B.). C.E. (0°–10°) ·001162 (E.). Smells like pine-apples, in which it occurs as well as in other fruits.

Allyl ether (140°) (Cahours a. Hofmann, *Tr.* 1857, 555; *A.* 102, 296); (145°) (Berthelot a. De Luca, *A.* 100, 360).

Propyl ether (143° cor.). S.G. $\frac{0}{4}$ ·8930 (E.); ^{15} 1·879 (Linnemann, *A.* 161, 53). S.V. 173·85 (S.). C.E. (0°–10°) ·001077 (E.).

Iso-propyl ether. (128°). S.G. ^{0} ·879; ^{13} ·865 (Silva, *A.* 153, 135).

n-Butyl ether (165° cor.). S.G. $\frac{0}{0}$ ·8878 (G.); ^{12} ·876 (Linnemann, *A.* 161, 195); ^{0} ·889; ^{20} ·872 (Lieben a. Rossi, *A.* 158, 170). S.V. 197·8 (G.). C.E. (0°–10°) ·00105 (G.).

Iso-butyl ether (158°) (S.); 157° (E.). S.G. $\frac{0}{4}$ ·8818 (E.); ^{0} ·880; ^{16} ·866 (Grünzweig, *A.* 162, 207). S.V. 197·66 (S.); 200·53 (E.). C.E. (0°–10°) ·001093 (E.). *Velocity of bromination*: Urech, *B.* 13, 1693.

n-Amyl ether (184·8°). S.G. $\frac{0}{0}$ ·8832. C.E. (0°-10°) ·00099. S.V. 222·3 (Ga.).

Iso-amyl ether. (176°) (Delffs, *A.* 92, 278); (178·6°) (E.). S.G. $\frac{0}{4}$ ·8823 (E.). S.V. 221·52 (E.). C.E. (0°–10°) ·001014 (E.).

Hexyl ether. (205°). S.G. $\frac{0}{0}$ ·8825. C.E. (0°–10°) ·00096. S.V. 246·4 (Ga.). From *Heracleum* (Franchimont a. Zincke, *A.* 163, 198).

Heptyl ether (225°). S.G. $\frac{0}{0}$ ·8827. C.E. (0°–10°) ·00093. S.V. 270·2 (Gartenmeister).

Octyl ether. (245°) (R.); (242°) (G.). S.G. $\frac{0}{0}$ ·8794. C.E. (0°–10°) ·00091. S.V. 295·6 (G.). From *Pastinaca sativa* (Renesse, *A.* 166, 80).

Cetyl ether. [20°]. (c. 265°) at 200 m.m. S.G. ^{20} ·856 (Dollfus, *A.* 131, 285).

Ethylene ether *v.* GLYCOL.

Ethylidene ether *v.* *Di-butyryl ortho-*ALDEHYDE p. 106.

Glyceryl ether *v.* GLYCERIN.

Amide $C_3H_7.CONH_2$. [115°]. (216°). Prepared by heating ammonium butyrate under pressure at 230°; the yield is 75 p.c. (Chancel, *A.* 52, 294; Buckton a. Hofmann, *C. J.* 9, 241; *B.* 15, 982).—$Hg(C_4H_8NO)_2$.

Anilide $C_3H_7.CO.NH(C_6H_5)$. [92°]. Pearly plates (from dilute alcohol). Sol. ether. Formed by heating butyramide, butyric anhydride, or

chloride with aniline (Gerhardt, *A. Ch.* [3] 37, 329; Kelbe, *B.* 16, 1200).

Chloride $C_3H_7.COCl$. Mol. w. 106·5. (101°). S.G. $\frac{20}{4}$ 1·0277. μ_β 1·4178. R_∞ 41·43 (Brühl, *A.* 203, 19). From butyric acid (96 pts.) and PCl_3 (100 pts.) (Burcker, *A. Ch.* [5] 26, 468; Linnemann, *A.* 161, 179). Converted by sodium-amalgam into dibutyryl $(C_4H_7O)_2$. Al_2Cl_6 forms crystalline $C_{12}H_{18}O_3$ [107°] 'butyro-butyryl-butyric anhydride.' NaOH forms $C_{12}H_{19}NaO_4$ (Combes, *C. R.* 104, 853).

Bromide $C_4H_7O.Br$. (128°) (Berthelot, *J.* 1857, 344).

Iodide $C_4H_7O.I$ (147°) (Cahours, *A.* 104, 111).

Anhydride $(C_4H_7O)_2O$. (192°). S.G. $\frac{12}{}$ ·978. V.D. 5·38 (obs.). From sodium butyrate (4 pts.) and $POCl_3$ (2 pts.) or BzCl ($2\frac{1}{2}$ pts.) (Gerhardt, *A.* 87, 155). Also from butyryl chloride and butyric acid (Linnemann, *A.* 161, 179). Heated with sodium butyrate at 180° it forms di-propyl-ketone (Perkin, *C. J.* 49, 325).

Peroxide $(C_4H_7O)_2O_2$. From butyric anhydride and Bz_2O_2. Oil (Brodie, *Pr.* 12, 655).

Nitrile $C_3H_7.CN$. *Propyl cyanide.* Mol. w. 69. (119°). S.G. $\frac{12}{}$ ·795. Formed by distilling the amide or ammonium butyrate with P_2O_5 (Dumas, *A.* 64, 334; Henke, *A.* 106, 272).

Isobutyric acid $(CH_3)_2CH.CO_2H$. Mol. w. 88. (153° cor.). S.G. $\frac{15}{15}$ ·9539; $\frac{25}{25}$ ·9457 (Perkin, *C. J.* 45, 487); $\frac{20}{4}$ ·9490 (Brühl); $\frac{0}{0}$ ·9651 (Zander). C.E. (0°–10°) ·00110 (Z.). S. 20 at 20°. M.M. 4·479 at 17·8° (P.). S.V. 108·57 (R. Schiff, *A.* 220, 105). μ_β 1·3979. R_∞ 35·48 (B.). S.H. ·435 at 0° (Schiff, *A.* 234, 300). *Heat of solution* 973. *Heat of neutralisation in dilute solution* 13989 (Gal a. Werner, *Bl.* [2] 46, 801). *Vapour-pressure*: Richardson (*C. J.* 49, 7̣63).

Occurrence.—1. In St. John's bread, the fruit of *Ceratonia siliqua* (Grünzweig, *A.* 158, 117; 162, 193).—2. In the root of *Arnica montana* (Sigel, *A.* 170, 345).—3. As an ether (isobutylic?) in Roman oil of chamomile (Kopp, *A.* 195, 85; Köbig, *A.* 195, 96).—4. In human excrement (Brieger, *B.* 10, 1029).

Formation.—1. From iso-propyl cyanide and potash (Markownikoff, *A.* 138, 361).—2. By saponifying di-methyl-aceto-acetic ether (Frankland a. Duppa, *A.* 138, 337).—3. Aqueous calcium butyrate which had been heated and cooled in a sealed tube 30 or 40 times in 10 years was found to have changed to the extent of 10 p.c. into calcium isobutyrate (Erlenmeyer, *A.* 181, 126).—4. By the oxidation of pyroterebic acid (Williams, *B.* 6, 1094).

Preparation.—By adding $K_2Cr_2O_7$ (4 pts.) to a cold mixture of isobutyl alcohol (3 pts.), H_2SO_4 ($5\frac{1}{2}$ pts.) and water (15 pts.). Isobutyl isobutyrate separates. It is distilled with moist potash, and the potassium salt is distilled with strong H_2SO_4 (Pierre a. Puchot, *A. Ch.* [4] 28, 366).

Properties.—Unpleasant smelling liquid.

Reactions.—1. *Oxidised* by CrO_3 mixture at 140° to CO_2, acetone (Popoff, *Z.* 1871, 4) and acetic acid (Erlenmeyer, *Z.* [2] 7, 57).—2. *Oxidised* by $KMnO_4$ in alkaline solution, to β-oxy-isobutyric acid, $(CH_3)_2C(OH).CO_2H$, according to Richard Meyer's rule that when the group CH is united to three carbon atoms it may be oxidised to C.OH.—3. Calcic isobutyrate on *distillation* gives di-isopropyl-ketone, with smaller quantities of methyl *tert*-butyl ketone, isobutyric aldehyde, and isobutyric acid (Barbaglia a. Gucci, *G.* 11, 84).

Salts.—More soluble than those of *n*-butyric acid.—CaA'_2aq: small plates. S. (of CaA'_2) 20 at 0°; 18 at 80°; 25 at 100°.—CaA'_25aq: long monoclinic prisms (Chancel a. Parmentier, *C. R.* 104, 477).—SrA'_25aq. S. 44 at 17° (hydrated) (Grünzweig).—$BaA'_2\frac{1}{2}aq$. Monoclinic.—BaA'_2HA' [74°] (Mixter, *Am.* 8, 346).—$BaA'_2Ba(C_4H_7O_2)_2aq$.—ZnA'_2aq. S. (hydrated). 17 at 20°.—PbA'_2. S. 9 at 16°. Trimetric plates. Melts under hot water.—AgA'. S. ·93 at 16°. Plates.

Methyl ether. (92°). S.G. $\frac{0}{4}$ ·9112 (Elsässer, *A.* 218, 332). C.E. (0°–10°) ·001223 (E.). S.V. 126·5. H.F. p. 109,660. H.F. v. 116,760 (*Th.*).

Ethyl ether. (110°). S.G. $\frac{0}{4}$ ·8904 (E.); $\frac{15}{15}$ ·8758; $\frac{25}{25}$ ·8670 (Perkin, *C. J.* 45, 487). M.M. 6·479 at 21·8° (P.). C.E. (0°–10°) ·001156 (E.). S.V. 148·86 (E.); 150·68 (Schiff, *A.* 220, 333).

Propyl ether. (135°). S.G. $\frac{0}{4}$ ·8843 (E.). C.E. (0°–10°) ·001039 (E.). S.V. 173·7 (E.); 174·2 (S.).

Iso-propyl ether (120°). S.G. $\frac{0}{}$ ·879 (Pribram a. Handl, *M.* 2, 691).

Iso-butyl ether. (146·6°) (E.); (149°) (S.). S.G. $\frac{0}{4}$ ·8750 (E.). C.E. (0°–10°) ·000994 (E.). S.V. 198·2 (S.); 196·0 (E.).

Iso-amyl ether. (169°) (E.). S.G. $\frac{0}{4}$ ·8760. C.E. (0°–10°) ·001031. S.V. 223·04.

Benzyl ether v. p. 493.

Amide [129°]. (c. 218°). Prepared by heating ammonium isobutyrate at 230° under pressure; the yield is 90 p.c. (Hofmann, *B.* 15, 982; *cf.* Letts, *B.* 5, 672; Münch, *A.* 180, 340; and *Di-iso*-BUTYRAMIDE).

Bromo-amide $C_3H_7.CO.NHBr$. [92°]. Prepared by the action of bromine and KOH on isobutyramide (Hofmann, *B.* 15, 755). Large colourless needles, sol. ether, sl. sol. water. Decomposed by caustic alkalis into propylamine, HBr, and CO_2, but by carbonated alkalis the reaction stops half way with production of propyl cyanate.

Iso-propyl-amide PrCO.NHPr. [102°]. (210°). Formed by the action of acetyl chloride on di-isopropyl acetoxim (Meyer and Warrington, *C. J.* 51, 685). Also by the action of isobutyryl chloride on isopropylamine. Colourless transparent needles v. sol. alcohol and ether, m. sol. water. Sublimes at ordinary temperatures and distils without decomposition. Is decomposed by prolonged boiling with alcoholic potash into isobutyric acid and isopropylamine.

Anilide $C_3H_7.CO.NHC_6H_5$. [103°]. From isobutyric acid and aniline (Norton, *Am.* 7, 116). Prisms.

p-Bromo-anilide $C_3H_7.CO.NH.C_6H_4Br$ [1:4]. [128°]. From the preceding and Br (N.).

Chloride $C_3H_7.COCl$. (92°) (Markownikoff, *Z.* 1866, 501). S.G. $\frac{20}{4}$ 1·0174 (Brühl, *A.* 203, 20). μ_β 1·4135. R_∞ 41·41 (B.). $ZnMe_2$ (1 mol.) followed by water converts isobutyryl chloride into a ketone $C_{10}H_{18}O$ (190°). S.G. $\frac{2}{}$ ·870 (Pawlow, *A.* 188, 139). $ZnMe_2$ (2 mols.) followed by water forms tertiary butyl alcohol and sometimes a ketone $C_{12}H_{22}O$ (218°). S.G. $\frac{0}{}$ ·864.

Bromide (117°).

Anhydride $(C_4H_7O)_2O$. (182°). S.G. $\frac{13}{13}$ ·9574 (Markownikoff, *Z.* 1866, 501; Tönnies a. Staub, *B.* 17, 850).

Nitrile $(CH_3)_2CH.CN$. (108°). From isopropyl iodide, KCN, and alcohol (Markownikoff, *Bl.* 1866, 53). From isobutyric acid and potassium sulphocyanide (Letts, *B.* 5, 669).

n-BUTYRIC ALDEHYDE C_4H_8O *i.e.* $CH_3.CH_2.CH_2.CHO$. (74°). Mol. w. 72. S.G. $\frac{20}{4}$ ·8170 (Brühl). μ_β 1·3893. R_∞ 32·93. S. 3·7. Got by distilling calcium butyrate with calcium formate (Linnemann, *A.* 161, 186; Lipp, *A.* 211, 355). From caseïn by oxidation with H_2SO_4 and MnO_2 (Guckelberger, *A.* 64, 39).

Reaction.—Aqueous NaOH and NaOAc form oily $C_8H_{14}O$ (173°). It is probably $Pr.CH_2.CH:CEt.CHO$ as it reacts with phenylhydrazine and combines with bromine (Raupenstrauch, *M.* 8, 108).

Ammonia compound $(CH_3)_2CH.CH(OH)(NH_2)$ $3\frac{1}{2}$aq. [31°]. Trimetric pyramids. V. sl. sol. water, v. sol. alcohol, m. sol. ether. Deliquesce above 4°, giving off water.

Bisulphite compound $C_4H_8ONaHSO_3$ (Juslin, *B.* 17, 2505; Kahn, *B.* 18, 3364).

Butyraldines. Dibutyraldine $C_8H_{17}NO$ and tetra-butyraldine $C_{16}H_{29}NO_2$ are formed by the protracted action of alcoholic ammonia on butyric aldehyde (Schiff, *A.* 157, 352). Butyraldine, on distillation, gives para-coniine $C_8H_{15}N$.

Butyral C_4H_8O (?) (95°). S.G. $\frac{22}{}$ ·821. A product of distillation of calcic butyrate (Chancel, *A. Ch.* [3] 12, 146; Limpricht, *A.* 90, 111; 93, 241). Reduces Ag_2O. Does not combine with NH_3. Combines with $NaHSO_3$.

Reactions.—1. Air or Ag_2O forms butyric acid.—2. *Chlorine* forms C_4H_7ClO (141°) and $C_4H_6Cl_2O$ (200°).—3. PCl_5 forms C_4H_7Cl (c. 100°).

Isobutyric aldehyde $(CH_3)_2CH.CHO$. (64°). S.G. $\frac{15}{15}$ ·7972; $\frac{25}{25}$ ·7879 (Perkin, *C. J.* 45, 476); $\frac{20}{4}$ ·7938 (Brühl, *A.* 203, 18). S. 11 at 20°. μ_β 1·3777. R_∞ 32·89. H.F.p. 61,340. H.F.v. 59,310. M.M. 4·321 at 19·3°.

Formation.—1. From isobutyl alcohol by chromic mixture (Pfeiffer, *B.* 5, 699; Michaelson, *A.* 133, 182; Pierre a. Puchot, *C. R.* 70, 434).—2. By heating iso-butylene bromide, $(CH_3)_2CHBr.CHBr$, with water (20 vols.) at 160° (Linnemann a. Zotta, *A.* 162, 36).—3. By distilling calcium isobutyrate (Popoff, *B.* 6, 1255; Barbaglia a. Gucci, *B.* 13, 1572).—4. By distilling calcium isobutyrate with calcium formate (Linnemann a. Zotta, *A.* 162, 7).—5. By distilling colophony (Tilden, *B.* 13, 1604).

Preparation.—A mixture of conc. aqueous $K_2Cr_2O_7$ with an equal volume of H_2SO_4 is slowly run into a flask containing iso-butyl alcohol (100 g.) and water (200 g.) until the layer of alcohol has disappeared. The product is distilled. The yield is 55 p.c. of the theoretical (W. H. Perkin, jun., *C. J.* 43, 91; *cf.* Fossek, *M.* 4, 660).

Properties.—Pungent liquid. Forms a compound with $NaHSO_3$ from which it is separated by potash without change.

Reactions.—1. By the action of potash (4 g.) in alcohol (140 g.) upon the aldehyde (50 g.) the following bodies may be obtained; isobutyric acid, an acid $C_{12}H_{22}O_3$ (245°-255°) and an aldehyde $C_{12}H_{22}O_2$.—2. If more potash (8 g.) and a higher temperature be used, the neutral products are: $C_{12}H_{22}O_2$, $C_{16}H_{30}O_3$?, $C_{20}H_{38}O_4$, $C_{24}H_{44}O_4$ and $C_{28}H_{48}O_5$ (W. H. Perkin, jun., *C. J.* 43, 101).—3. Aqueous potash forms an acid $C_8H_{16}O_3$ [75°-80°], a crystalline body $C_8H_{18}O_2$ [90°], and di-oxy-octane (Fossek, *M.* 3, 622).—4. PCl_5 gives chloro-isobutylene $Me_2C:CHCl$ (68°) and di-chloro-isobutane (104°) $Me_2CH.CHCl_2$ (Oeconomides, *C. R.* 92, 884).—5. H_2S and aqueous ammonia form isobutyraldine $C_{12}H_{25}NS_2$ (Pfeiffer, *B.* 5, 700). 6. CS_2 and conc. NH_3Aq give $NH_2.CS.SN(C_4H_9)_2$ [91°]. Prisms, insol. water, v. sol. alcohol.—7. Alcohol and HCl followed by NaOEt form di-ethyl-ortho-isobutyric aldehyde $CMe_2CH\ CH(OEt)_2$ (135°). S.G. $\frac{12}{}$ ·996, V.D. 143·5, and, when some water is also present, a compound $C_{10}H_{20}O$ (223°) (Oeconomides, *Bl.* [2] 36, 210; *C. R.* 92, 886).—8. Gives with *ammonia* a crystalline compound $(C_4H_8)_7N_6H_6O$ (Lipp, *A.* 205, 1; 211, 344; *B.* 13, 906; 14, 1746).

$$7C_3H_7CHO + 6NH_3 = 6H_2O + (C_3H_7CH)_7N_6H_6O.$$

When the product, 'oxy-hepta-iso-butylidene-amine' [32°], is heated, it first splits up into $2NH_3$, C_4H_8O and $2(C_4H_8)_3N_2$. The latter is hydro-butyramide, an oil, nearly insoluble in water, v. sol. alcohol or ether. If quickly heated it distils at 154°, but if heated slowly it splits up into NH_3 and $C_8H_{15}N$. *Hydro-butyramide* or tri-isobutylidene-diamine is not affected by boiling KOH, but dilute HCl splits it up into butyric aldehyde and NH_3. It is, therefore, $C_4H_8:N.C_4H_8.N:C_4H_8$. Dry HCN added to its ethereal solution forms the dihydrochloride of $(Cy.C_4H_8.NH)_2C_4H_8$ a body that is decomposed by water into isobutyric aldehyde and amido-valero-nitrile. When hydro-butyramide is slowly heated it does not, like hydro-benzamide, change into an isomeride, but splits up, giving $C_8H_{15}N$. This compound, 'iso-butenyl-butylidene-amine,' is a liquid (145°-147°) at 715 mm., nearly insoluble in water, miscible with alcohol or ether. It is not affected by aqueous KOH, but acids split it up into isobutyric aldehyde and NH_3. It would thus appear to be $(CH_3)_2CH.CH:N.CH:C(CH_3)_2$. It combines with Br, forming $C_8H_{15}NBr_2$, a body that, when kept for a long time, and then treated with water, gives NH_4Br, isobutyric aldehyde and bromo-isobutyric aldehyde, or rather a polymeride of the latter [129°]. If $C_8H_{15}NBr_2$ be at once treated with water, the unstable liquid bromo-butyric aldehyde is probably formed (Lipp.).

Oxim $C_3H_7.CH:N(OH)$. [139°]. Colourless liquid. Sol. water. Formed by the action of an aqueous solution of hydroxylamine on isobutyric aldehyde (Petraczek, *B.* 15, 2784).

Description of condensation products, obtained as above (W. H. Perkin, jun., *C. J.* 43, 90).

Acid $C_{12}H_{22}O_3$ (245°-255°). Brownish oil. Reduces ammoniacal Ag_2O.

Compound $C_{12}H_{22}O_2$ (154°-157°). Oil. Ethereal odour. Reduces ammoniacal Ag_2O. Combines slowly with $NaHSO_3$. Decomposes on prolonged heating. Is probably Urech's $C_8H_{14}O$ (*B.* 12, 191). With Na and wet ether, it is reduced to $C_{12}H_{26}O_2$ (170°-175°), an alcohol (?) which does not combine with $NaHSO_3$.

Compound $C_{20}H_{38}O_4$ (223°-225°). Oil Smells of camphor. Very slowly combines with $NaHSO_3$, forming needles. Reduces ammoniacal Ag_2O. V.D. 167 (Theory 342). With Ac_2O it

forms $C_{22}H_{37}AcO_4$ (240°–242°). Oil, which with Ac_2O at 200° gives $C_{20}H_{36}Ac_2O_4$ (248°–252°). When saponified by KOH a body $C_{20}H_{42}O_4$ (c. 220°) is formed.

Compound $C_{20}H_{44}O_4$ (250°–253°). Oil. V.D. (air = 1) 12·9 (Theory 13·7).

Compound $C_{28}H_{48}O_3$ (227°–229°) at 100 mm. Thick oil. Decomposed when heated under atmospheric pressure.

Di-isobutyric di-aldehyde $C_8H_{16}O_2$. (138°) at 18 mm. V.D. 5·2 (calc. 5·0). This polymeride of isobutyric aldehyde is obtained, together with octenoic aldehyde (?) $C_8H_{14}O$ (150°) by heating isobutyric aldehyde with conc. aqueous NaOAc at 150° (Fossek, *M.* 2, 622). It is an oil, sol. alcohol and ether, forming a crystalline compound with $NaHSO_3$.

Iso-butyric paraldehyde $(C_4H_8O)_3$. [60°]. (195°). V.D. (H=1) 104·8. From iso-butyraldehyde by H_2SO_4, HCl, PCl_5, Cl, Br, or I (Barbaglia, *B.* 5, 1052; 6, 1064; *G.* 16, 430; Demtschenko, *B.* 6, 1176). Needles (from water or by sublimation). Difficultly attacked by oxidising agents (Urech, *B.* 12, 1749). Does not combine with $NaHSO_3$ or react with NH_3. At 150° it partially changes to ordinary isobutyric aldehyde.

Iso-butyric poly-aldehyde $(C_4H_8O)_n$. S.G. $\frac{24}{}$ ·969. Prepared by leaving isobutyric aldehyde in contact with dry Na_2CO_3. Thick liquid. Sl. sol. water. Decomposed on distillation, with separation of water and formation of isobutyric aldehyde and condensation products (Urech, *B.* 12, 191, 1744; 13, 483, 590).

BUTYRIN *v.* GLYCERIN.

BUTYRO-CHLORAL *v.* TRI-CHLORO-BUTYRIC ALDEHYDE.

BUTYRO-COUMARIC ACID *v.* OXY-PHENYL-PENTENOIC ACID.

BUTYRO-CREATININE *v.* METHYL-AMIDO-BUTYRIC ACID.

BUTYRO-FURONIC ACID $C_9H_{12}O_5$ *i.e.* $CO_2H.CH:CH.CO.CH_2.CH_2.CH_2.CH_2.CO_2H$ (?). [142°]. Prepared by treating furfurvaleric acid with bromine-water and subsequent action of silver oxide. White crystals. Sol. water and alcohol, sl. sol. ether. By HI and P it is reduced to azelaic acid (Toennies, *B.* 12, 1200).

BUTYRO-LACTONE *v.* γ-OXY-BUTYRIC ACID.

BUTYROLIC ACID *v.* TETROLIC ACID.

BUTYRONE *v.* DI-PROPYL-KETONE.

BUTYRONITRILE *v. Nitrile of* BUTYRIC ACID.

BUTYRO-PINACONE $C_{14}H_{30}O_2$ *i.e.* $CPr_2(OH).CPr_2(OH)$. *Di-oxy-tetradecane.* [68°]. (260°). From di-propyl-ketone, water, and Na (Kurtz, *A.* 161, 215). Crystals, smelling of camphor, sl. sol. water.

BUTYRO-THIÉNONE *v.* THIËNYL PROPYL KETONE.

DI-BUTYRYL $C_8H_{14}O_2$ *i.e.* Pr.CO.CO.Pr. *Di-propyl di-ketone.* (245°–260°). From butyryl chloride and sodium-amalgam or zinc (Freund, *A.* 118, 35). Yellow oil. Boiled with potash it forms butyrate of potassium and a liquid $C_7H_{14}O$ which does not unite with NH_3 or $NaHSO_3$.

Mono-oxim $C_3H_7.CO.C(NOH).C_3H_7$: thick oil; can be distilled in small quantity without decomposition. A *di-oxim* has not been obtained (Münchmeyer, *B.* 19, 1846).

BUTYRYL-ACETOPHENONE $C_6H_5.CO.CH_2.CO.C_3H_7$. *Benzoyl-methyl-propyl-ketone.* (174° at 24 mm.). S.G. 1·061 at 15°. Colourless oil. Formed from acetophenone and butyric ether by EtONa (Beyer a. Claisen, *B.* 20, 2181).

Isobutyryl-acetophenone $C_6H_5.CO.CH_2.CO.C_3H_7$. *Benzoyl-methyl-iso-propyl-ketone.* (170° at 26 mm.). Colourless liquid. Formed from acetophenone and isobutyric ether by EtONa (Beyer a. Claisen, *B.* 20, 2181).

BUTYRYL-AMIDO-BENZOIC ACID $PrCO.NH.C_6H_4.CO_2H$. [209°]. From *n*-butyric ether (20 c.c.) and *m*-amido-benzoic acid (10 g.) at 180° in sealed tubes (Pellizzari, *A.* 232, 148). Sol. water and alcohol.

BUTYRYL BROMIDE *v.* BUTYRIC ACID.

BUTYRYL CHLORIDE *v.* BUTYRIC ACID.

BUTYRYL CYANAMIDE *v.* CYANAMIDE.

***n*-BUTYRYL CYANIDE** C_5H_7NO *i.e.* PrCO.CN. (133°–137°). From AgCN and PrCOCl (E. Moritz, *C. J.* 39, 16).

***n*-Di-butyryl di-cyanide** $(PrCO)_2(CN)_2$ (c. 234°). By-product in preparation of above.

Iso-butyryl cyanide Pr.CO.CN. (117°–120°). From PrCO.Cl (40 g.) and AgCN (50 g.). Bad yield (E. Moritz, *C. J.* 39, 13). The greater part of the product is **di-iso-butyryl di-cyanide** (226°–228°). S.G. ·96.

BUTYRYL IODIDE *v.* BUTYRIC ACID.

BUTYRYL-MALONIC ETHER $C_3H_7.CO.CH(CO_2Et)_2$. (247°–252°). Formed by the action of butyryl chloride upon sodio-malonic ether. By nitrous acid it is converted into iso-nitroso-butyryl-acetic ether (Lang, *B.* 20, 1326).

BUTYRYL PEROXIDE *v.* BUTYRIC ACID.

BUTYRYL-PROPYL-UREA *v. Butyryl derivative of* PROPYL-UREA.

BUTYRYL SULPHOCYANIDE (180°). From butyryl chloride and lead sulphocyanide. Decomposes when boiled (Miquel, *A. Ch.* [5] 11 295).

BUTYRYL-UREA *v.* UREA.

BUXEINE. An alkaloid extracted by dilute oxalic acid from the bark of the box-tree *Buxus sempervirens.* Yellowish-white crystalline substance, sol. alcohol and ether, sl. sol. water. HNO_3 gives a greenish-yellow colouration turning brick-red. H_2SO_4 gives a blood-red colour. Chromic acid mixture gives an orange pp. (Alessandri, *G.* 12, 96). It is perhaps identical with buxine. Barbaglia finds four alkaloids in the leaves and twigs of the box: buxine, parabuxine, buxidine, and buxinidine (*G.* 13, 249; *B.* 17, 2655).

BUXINE $C_{19}H_{21}NO_3$(?). An alkaloid extracted by dilute oxalic acid from the leaves of the box tree. White crystalline substance, sol. alcohol and ether, sl. sol. water. HNO_3 gives a purple-red colouration. H_2SO_4 gives a brick-red colour. Chromic acid mixture gives a canary-yellow pp. (Alessandri, *G.* 12, 96; Barbaglia, *B.* 4, 757; Fauré, *J. Ph.* 16, 428; Couerbe, *J. Ph.* 1854, 51). According to Walz (*J.* 1860, 548) buxine is identical with bebeerine (*q.v.*).

Parabuxine $C_{26}H_{48}N_2O$ (?) An alkaloid occurring in both leaves and bark of the box tree. It is a reddish-purple amorphous resin, sol. water and alcohol, insol. ether. HNO_3 gives a permanent greenish-yellow colouration. H_2SO_4 gives a greenish-yellow colour becoming dark. Chromic acid mixture gives no pp.—$B''H_2SO_4$.—$B''2HCl$.—$B''H_2PtCl_6$ (Pavesi a. Rotondi, *G.* 4, 192; Alessandri).

C

CACAO *v.* THEOBROMINE.

CACODYL *v.* p. 318.

CACOSTRYCHNINE $C_{21}H_{22}N_5O_{10}$. A product of the action of HNO_3 on strychnine (*q. v.*). Golden needles (from dilute HNO_3) or hexagonal plates (from conc. HClAq). Sl. sol. most menstrua, sol. alkalis, forming red solutions.—$B'_2H_2PtCl_6$ (Claus a. Glassner, *B.* 14, 773).

CACOTHELINE $C_{20}H_{22}N_4O_9$. A product of the action of HNO_3 on brucine (*q. v.*). Orange laminæ (containing aq). Weak base; sol. alkalis, v. sl. sol. hot water, insol. alcohol and ether.—B'BaO 7aq.—$B'_2H_2PtCl_6$ (Strecker, *A.* 91, 76; *C. R.* 39, 52; Rosengarten, *A.* 65, 111; Claus a. Röhre, *B.* 14, 765).

CADAVERIC ALKALOIDS *v.* PTOMAÏNES.

CADET'S FUMING LIQUID *v.* p. 318.

CADMIUM. Cd. At. w. 111·7. Mol. w. 111·7; gaseous molecule is monatomic. [320°] (Person, *A. Ch.* [3] 27, 250; Rudberg, *P.* 71, 460; v. Riemsdyk, *C. N.* 20, 32). (763°–772°) (Carnelley a. Williams, *C. J.* 33, 284). S.G. (molten) 8·65, (hammered) 8·8 (Stromeyer, *S.* 22, 362; Schröder, *P.* 106, 226; 107, 113; Matthiessen, *P.* 110, 21, &c.). V.D. 55·8 (Deville a. Troost, *C. R.* 52, 920). S.H. (0°–100°) ·0548 (Bunsen, *P.* 141, 1), ·0567 (Regnault, *A. Ch.* [3] 26, 268). C.E. (linear, 0°–100°) ·003323; (cubical for 1°) ·000094 (Kopp, *A.* 81, 32; Matthiessen, *P.* 130, 50; Fizeau, *C. R.* 68, 1125). T.C. (Ag=100) 20·06 (Lorenz, *W.* 13, 422). E.C. (Hg at 0°=1) at 0°, 13·46; at 100°, 9·5 (Lorenz, *W.* 13, 422 a. 582). Heat of fusion 13,660 (Person, *P.* 76, 426). S.V.S. abt. 12·8. Emission-spectrum characterised by lines 3609·6, 3465·4, 2747·7, 2572·2, 2313·6, 2288·9 (Hartley, *T.* 1884. 63).

Cd was discovered by Stromeyer in 1817 in a specimen of zinc carbonate (*S.* 21, 297; 22, 362; *v.* also Hermann, *G. A.* 59, 95). The name *cadmium* was derived from *cadmia fossilis* by which name zinc ore was then known.

Occurrence.—With Zn in various native sulphides, carbonates, and silicates, especially in the Silesian zinc ores (*v.* Damour, *J. pr.* 13, 354; Stadler, *J. pr.* 91, 359; Blum, *J.* 1858. 734; Bunsen, *A.* 133, 108). CdS occurs nearly pure as *Greenockite* at Bishopton in Renfrewshire.

Formation.—In the distillation of crude zinc oxide with charcoal; the greater part of the Cd distils over before the Zn.

Preparation. — ZnO containing CdO, or metallic Zn containing Cd, is dissolved in dilute H_2SO_4Aq or HClAq; the warm solution is saturated with H_2S; the CdS thoroughly washed and dissolved in conc. HClAq; most of the free HCl is removed by warming, the solution is diluted and filtered, and an excess of $(NH_4)_2CO_3$ is added; the pp. of $CdCO_3$ is well washed, dried, and strongly heated; the CdO thus produced is mixed with $\frac{1}{10}$ of its weight of pure powdered charcoal and heated in a retort of hard-glass or porcelain when pure Cd distils over (Stromeyer, *S.* 22, 362).

Properties.—White with slight blue tinge; very lustrous; soft, but harder than zinc; very malleable, ductile, and flexible; more tenacious than tin; crystallises easily in monometric forms, chiefly the octahedron (*v.* Kämmerer, *B.* 7, 1724; also G. Rose, *P.* 85, 293). Vapour is yellow. Cd does not decompose water even at 100°; but if Cd vapour and steam are passed through a hot tube the steam is decomposed (Regnault, *A. Ch.* 62, 351). Cd oxidises slowly on the surface by exposure to air; when heated in air it burns to CdO. The atomic weight of Cd has been determined (1) by finding the V.D. of, and by analysing, $CdBr_2$ (Meyer, *B.* 12, 1292; Dumas *A. Ch.* [3] 55, 158; Huntington, *P. Am. A.* 17, 28); analyses of CdC_2O_4 (Lenssen, *J. pr.* 79, 281); reduction of $CdSO_4$ to CdS (v. Hauer, *C. C.* 1857. 897); analyses of CdO (Stromeyer, *S.* 22, 366); (2) by determining the S.H. of Cd (Bunsen, *P.* 141, 1; Regnault, *A. Ch.* [3] 26, 268); (3) by comparing, as regards crystalline form and general reactions, salts of Cd with salts of Zn, Be, Mg, and Hg. In the gaseous molecule $CdBr_2$ (this is the only compound of Cd whose V.D. has been determined) the atom of Cd is divalent. The gaseous molecule of Cd is monatomic. Cd is a distinctly metallic element; it acts on HClAq, H_2SO_4Aq, &c., evolving H and forming salts of the form CdX_2 where $X_2 = Cl_2$, Br_2, SO_4, CO_3, &c.; many of these salts combine with the similar salts of the more positive metals (K, Ca, Mg, &c.) to form double salts; but few basic salts of Cd are known, the most marked are derived from such weak acids as H_2CrO_4, H_3BO_3, &c. No compound of Cd exhibits any acidic functions. CdO_2H_2 acts towards acids as a salt-forming hydroxide; its heat of neutralisation by H_2SO_4Aq is about the same as that of the corresponding hydroxide of Mn, Ni, Co, Fe, or Zn, $[CdO^2H^2Aq, H^2SO^4Aq] = 23,830$ (*v. Th.* 1, 339 a. 436). CdO_2H_2 is dehydrated by heat; the oxide CdO is not converted to CdO_2H_2 by direct addition of H_2O. Cadmium is closely related to Zn, it is less positive than that metal; it is also related to Mg on one hand and to Hg on the other (*v.* MAGNESIUM GROUP OF ELEMENTS).

Reactions.—1. Heated in *air*, or O, CdO is produced. — 2. Heated nearly to redness in *bromine*, $CdBr_2$ is formed.—3. Aqueous solutions of *hydrochloric*, *sulphuric*, or *nitric*, *acids* are decomposed by Cd with formation of chloride, sulphate or nitrate of the metal. — 4. Heated with SO_2Aq to 200° CdS is formed (Geittner, *A.* 129, 354); possibly sulphite and thiosulphate are first formed (*v.* Schweitzer, *C. N.* 23, 293; Fordos a. Gélis, *A.* 50, 260).

Combinations.—Most compounds of Cd are formed from the oxide or other salt. Cd combines directly with the *elements* O, Cl, Br, I, P, S, Se, Te, and with many metals (*v.* CADMIUM, OXIDE OF, &c., and CADMIUM, ALLOYS OF).

Detection and Estimation.—Formation of the yellow sulphide, CdS, insoluble in dilute HClAq and also in solution of ammonium sulphide, characterises Cd salts. Cd is usually estimated by ppn. as $CdCO_3$ (by K_2CO_3Aq), the pp. is strongly heated, and the CdO is weighed. Separation from other metals may be effected

by repeated ppn. by H_2S, and solution of CdS in conc. HClAq. Cd may be ppd. as oxalate; on this fact is founded a volumetric method of estimation.

Cadmium, Alloys of. Usually prepared by melting the metals together. Several are characterised by low melting-points. An amalgam with Hg is formed at ordinary temperatures: by dissolving Cd in warm Hg, and pressing, a crystalline amalgam, having the composition Hg_2Cd_2, and S.G. 12·62, is formed; by completely saturating Hg with Cd, octahedral crystals of Hg_2Cd, melting at 75°, are produced (Gaugain, *C. R.* 42, 430; Regnauld, *C. R.* 51, 779; Crookewitt, *J. pr.* 102, 65 a. 129; Kopp, *A.* 46, 186). Easily fusible alloys with Bi agreeing in composition with the formulæ $BiCd_4$, $BiCd_2$, and BiCd, are known (Matthiessen, *P.* 110, 21). Various alloys of Cd with (1) Bi and Pb, (2) Bi, Pb and Sn, (3) Bi and Sn, are also known ([1] Wood, *D. P. J.* 164, 108; v. Hauer, *J. pr.* 94, 436: [2] Lipowitz, *D. P. J.* 158, 376: [3] Wood, *l.c.*). Alloys with Pb (Wood, *C. N.* 6, 135); Na (Sonnenschein, *J. pr.* 67, 169); Tl, and with Tl and Bi (Carstanjen, *J. pr.* 102, 65 a. 129); and Sn (Rudberg, *J.* 1817, 71), have been described. An arsenide, $AsCd_3$, is said to be obtained as a faintly red-coloured alloy, S.G. 6·26, by reducing the arsenate by KCN (Descamps, *C. R.* 86, 1022 a. 1065).

Cadmium, Arsenates of. $Cd_3(AsO_4)_2.3H_2O$, and $Cd_3H_2(AsO_4)_2.4H_2O$; *v.* ARSENATES, under ARSENIC, ACIDS OF.

Cadmium, Arsenide of. Cd_3As *v.* CADMIUM, ALLOYS OF.

Cadmium, Bromide of. $CdBr_2$. Mol. w. 271·2. [570°] (Carnelley, *C. J.* 33, 278). (806°–812°) (Carnelley a. Williams, *C. J.* 37, 126). S.G. $\frac{20°}{4°}$ 4·794 (Clarke, *Am.* 5. No. 4). H.F. $[Cd,Br^2] = 75,200$; $[Cd,Br^2,Aq] = 75,640$ (Thomsen).

Preparation.—By heating Cd to redness in Br vapour; or by dissolving $CdCO_3$ in HBrAq and subliming.

Properties and Reactions.—White, crystalline, non-hygroscopic, solid; soluble in water, ether, and alcohol; decomposed by HNO_3Aq (Bodeker a. Giesecke, *J.* 1860. 17; Croft, *P. M.* [3] 21, 355; Berthemot, *A. Ch.* 44, 387; Rammelsberg, *A.* 44, 267).

Combinations.—Dissolved in H_2O, and evaporated, yields long white needles of $CdBr_2.4H_2O$; these are dehydrated at 200° $[CdBr^2,4H^2O] = 7,730$ (Thomsen). $CdBr_2Aq$ and KBrAq mixed and evaporated yield $2CdBr_2.2KBr.H_2O$, and on further evaporation $CdBr_2.4KBr$. The double salts

$2CdBr_2.2NaBr.5H_2O$, and $CdBr_2.BaBr_2.4H_2O$, have also been obtained (v. Hauer, *J. pr.* 64, 477; 69, 121. Croft, *J. pr.* 68, 399). $CdBr_2$ absorbs NH_3 to form $CdBr_2.4NH_3$; all NH_3 is removed by heat. Conc. $CdBr_2Aq$ saturated with NH_3, and evaporated, gives crystals of $CdBr_2.2NH_3$ (Croft, *P. M.* [3] 21, 355; Rammelsberg, *A.* 44, 267).

Cadmium, Chloride of. $CdCl_2$. Mol. w. unknown; probably as represented by formula $CdCl_2$. [541°] (Carnelley, *C. J.* 33, 279). (861°–954°) (Carnelley a. Williams, *C. J.* 35, 564). S.G. $\frac{17°}{4°}$ 3·655 (Clarke, *Am.* 5, No. 4). S. (20°) 140; (100°) 150 (Kremers, *P.* 103, 57; 104, 133; 105, 360). H.F. $[Cd,Cl^2] = 93,240$; $[Cd,Cl^2,Aq] = 96,250$ (Thomsen).

Preparation.—By dissolving Cd in HClAq and heating to low redness the crystals of $CdCl_2.2H_2O$ which separate on evaporation.

Properties and Reactions.—Pearly, lustrous plates; white powder after exposure to air for some time. S. (20°–100°) abt. 140 (Kremers, *P.* 103, 57; 104, 133). Insoluble in conc. HClAq.

Combinations.—1. With *water* to form efflorescent prisms of $CdCl_2.2H_2O$; $[CdCl^2,2H^2O] = 2,250$ (Thomsen); best obtained by dissolving Cd, CdO, or $CdCO_3$ in HClAq, evaporating, and crystallising.—2. With *hydrochloric acid and water* to form $CdCl_2.2HCl.7H_2O$: obtained by passing HCl into $CdCl_2Aq$; easily decomposed in air with evolution of HCl; $[CdCl^2,2HCl,7H^2O] = 40,200$ (Berthelot, *C. R.* 91, 1024).—3. With *ammonia*, to form $CdCl_2.6NH_3$ and $CdCl_2.2NH_3$. $CdCl_2.6NH_3$ is obtained by passing NH_3 over $CdCl_2$, or by passing HCl into $CdCl_2Aq$ containing excess of NH_3 until the NH_3 is partly neutralised. Loses $4NH_3$ by exposure to air, leaving $CdCl_2.2NH_3$; this compound is also produced by exposing to air a solution of $CdCl_2$ in excess of warm NH_3Aq (Croft, *P. M.* [3] 21, 55; Schüler, *A.* 87, 34; v. Hauer, *J. pr.* 64, 477; *v.* also André, *C. R.* 104, 908).—4. With various *metallic chlorides* to form double salts. These salts have been prepared chiefly by Croft (*P. M.* [3] 21, 55), and v. Hauer (*J. pr.* 63, 432; 64, 477; 66, 176; 69, 121); their crystalline forms, and the thermal conductivities of some of them, have been determined by Grailich (*J.* 1858. 182), and v. Lang (*P.* 135, 29). These double compounds are obtained by evaporating mixed solutions of the two chlorides; the chief are:—

$2CdCl_2.2NH_4Cl.H_2O$;	$CdCl_2.BaCl_2.4H_2O$;
$CdCl_2.4NH_4Cl$;	$2CdCl_2.BaCl_2.5H_2O$;
$2CdCl_2.2KCl.H_2O$;	$2CdCl_2.SrCl_2.7H_2O$;
$CdCl_2.4KCl$;	$2CdCl_2.CaCl_2.7H_2O$;
$CdCl_2.2NaCl.3H_2O$;	$CdCl_2.2CaCl_2.12H_2O$;
	$CdCl_2.2MgCl_2.12H_2O$;
	$CdCl_2.MCl_2.12H_2O$
	when M = Co, Fe, Mg, Mn, or Ni;
	$CdCl_2.CuCl_2.4H_2O$.

5. With the *hydrochlorides of many organic bases* to form double salts; *e.g.* with toluidine $4(C_7H_9N.HCl).3CdCl_2.2H_2O$ (Williams, *C. C.* 1856. 47; Galletly, *C. C.* 1856. 606).

Cadmium, Cyanide of. $Cd(CN)_2$. Prepared by evaporating KCNAq with $CdCl_2Aq$ (*v.* CYANIDES).

Cadmium, Fluoride of. CdF_2. Mol. w. unknown; probably as represented by formula. [520°] (Carnelley, *C. J.* 33, 280). S.G. $\frac{22°}{4°}$ 5·994 (Clarke, *Am.* 5, No. 4). Hard, white, crystalline mass; by evaporating solution of CdO in HFAq; not easily soluble in water; much more soluble in HFAq (Berzelius, *P.* 1, 26). By dissolving CdO and oxide of Sn, Zr, or Mo in HFAq, and evaporating, the double compounds $CdF_2.SnF_2.6H_2O$, $2CdF_2.ZrF_4.6H_2O$, and $CdF_2.2ZrF_4.6H_2O$, were obtained by Marignac (*Ann. M.* [5] 15, 221; *A. Ch.* [3] 60, 257); and the double compound $CdF_2.MoO_2F_2.6H_2O$ by Delafontaine (*J.* 1867. 236).

Cadmium, Hydrated oxide of, $CdO.H_2O$ *v.* next article.

Cadmium, Hydroxide of, CdO_2H_2. A white, amorphous solid, obtained by adding KOHAq to a dilute aqueous solution of a Cd salt, washing with warm water, and drying at 100°-200° (Schaffner, *A.* 51, 168). According to Nicklès (*J. Ph.* [3] 12, 406) CdO_2H_2 is obtained in crystals by keeping Cd in contact with Fe in NH_3Aq. De Schulten (*C. R.* 102, 72) describes the formation of hexagonal crystals of CdO_2H_2, S.G. $^{15°}$ 4·79, by dissolving 10 grams CdI_2 in 150 c.c. H_2O mixed with 360 grams KOH containing 13 p.c. H_2O, heating till all is dissolved, and cooling. Thomsen gives the thermal value $[Cd,O,H^2O] = 65,680$; and the following values for the heat of neutralisation of solid CdO_2H_2 (*Th.* 3, 285):

Q	[M,QAq]	$M = CdO_2H_2$.
H_2SO_4	24,200	
$H_2N_2O_6$	20,620	
$H_2S_2O_6$	20,360	
H_2Cl_2	20,290	
H_2Br_2	21,560	
H_2I_2	24,210	

The quantity of heat produced with the three haloid acids increases as the atomic weight of the halogen increases; in this respect CdO_2H_2 is analogous to the corresponding compounds of Hg and Pb, and differs from those of Ba, Ca, Sr, and Mg. CdO_2H_2 loses H_2O at 300° (H. Rose, *P.* 20, 152); CdO is not hydrated by contact with H_2O; according to the thermal values given by Thomsen (*Th.* 3, 285; and *P.* 143, 354 a. 497) the reaction $CdO + H_2O = CdO_2H_2$ would require the expenditure of about 10,000 units of heat.

Cadmium, Iodide of. CdI_2. Mol. w. unknown, but probably as represented by the formula. [404°] (Carnelley, *C. J.* 33, 278). (708°-719°, with decomposition) (Carnelley a. Williams, *C. J.* 37, 126). S.G. $\frac{abt. 18°}{4°}$ 5·644, and 4·626 (*v. Preparation* a. *Properties*). H.F. $[Cd,I^2] = 48,830$; $[Cd,I^2,Aq] = 47,870$ (Thomsen). $V_t = V_o$ (1 + ·00008748*t*), *t* not greater than 40° (Fizeau, *C. R.* 64, 314). S. (20°) 92·6; (60°) 107·6; (100°) 133·3 (Kremers, *P.* 103, 57; 104, 133; 111, 60).

Preparation and Properties.—1. By heating together Cd and I, in the ratio Cd:I_2, in absence of air.—2. By digesting together Cd and I under water (Stromeyer, *S.* 22, 362).—3. By evaporating a solution of 20 parts KI and 15 parts $CdSO_4$ to dryness, dissolving in alcohol, and crystallising (Vogel, *N. R. P.* 12, 393).—4. By dissolving $CdCO_3$ in HIAq, decolourising by addition of clippings of Cd, and crystallising (Clarke, *Am.* 5, No. 4).—5. By dissolving Cd in HIAq, evaporating, and crystallising (Clarke, *l.c.*). According to Clarke (*l.c.*) CdI_2 exists in two forms; the normal salt is white, is unchanged by heating to 250°, and has S.G. 5·644; the other salt is brownish, loses weight even at 40°, and has S.G. 4·626. The conditions under which the less stable salt is formed have not yet been exactly determined; Clarke obtained it twice by the action of HIAq on Cd and on $CdCO_3$. The S.G. of the less stable salt increases by heating to 50° for some time. If the formula-weight CdI_2 is divided by the S.G., the results are, for the stabler salt 64·8, and for the less stable salt 79·2; now S.V.S. of Cd + S.V.S. of I_2 = 64·3 (Clarke, *l.c.*).

Combinations.—1. With *ammonia* to form $CdI_2.6NH_3$ and $CdI_2.2NH_3$; obtained as the corresponding $CdCl_2$ compounds (*q. v.*): both are decomposed by H_2O with ppn. of CdO_2H_2 (Rammelsberg, *P.* 48, 153).—2. With some *metallic iodides* to form double salts; Croft (*J. pr.* 68, 399) described $CdI_2.2KI.2H_2O$ (aqueous solution of this salt pps. most of the organic bases from plants; Marmé, *N. R. P.* 16, 306); $CdI_2.2NH_4I.2H_2O$; $CdI_2.2NaI.6H_2O$; $CdI_2.BaI_2.5H_2O$; and $CdI_2.SrI_2.8H_2O$. Clarke (*Am.* 5, No. 4) obtained $CdI_2.3HgI_2$ as gold-coloured plates.

Cadmium, Oxide of. CdO. Mol. w. unknown. S.G (amorphous) 6·95, (crystalline) 8·11 (Stromeyer, *S.* 22, 362; Werther, *J. pr.* 55, 118; Schüler, *A.* 87, 34; Sidot, *C. R.* 69, 201; Follenius, *Fr.* 13, 279). H.F. $[Cd,O] = 75,500$ (calculated from data given by Thomsen, *Th.* 3, 285; *P.* 143, 354 a. 497).

Preparation.—As a dark-brown, amorphous, infusible, powder, by burning Cd in air or O; or by strongly heating CdO_2H_2, or $CdCO_3$. As black-brown very small octahedra (or other forms of the monometric system), by strongly heating $Cd.2NO_3$, or $CdSO_4$ (Werther, *l.c.*; Schüler, *l.c.*; Herapath, *B. J.* 3, 109).

Properties &c.—Reduced to Cd by heating with C. At red heat Cl forms $CdCl_2$. Readily combines with CO_2 forming $CdCO_3$. Dissolves in aqueous acid with production of Cd salts. Thomsen (*P.* 143, 354 a. 497) gives the thermal values, $[CdO,H^2SO^4Aq] = 14,240$ for crystalline CdO, and 14,510 for amorphous CdO.

Marchand (*P.* 38, 145) supposed that a lower oxide than CdO was formed when CdC_2O_4 was heated; but Vogel's experiments (*J.* 1855. 390) seem to prove that the substance was a mixture, in varying proportions, of CdO and Cd.

By the action of H_2O_2Aq (about 3 p.c. H_2O_2) on moist CdO_2H_2, Haas (*B.* 17, 2249) obtained an oxide of Cd containing more O than CdO. Analyses gave results agreeing fairly with the formula Cd_3O_5, in one case with Cd_4O_7. These results were confirmed by Bailey (*C. J.* 49, 484) who obtained Cd_3O_5 by the action of H_2O_2Aq on $CdSO_4Aq$ followed by addition of NH_3Aq. The pp. obtained by these methods may have been a mixture, or possibly a loose compound, of CdO and CdO_2 (*v.* Haas, *l.c.* 2255).

Cadmium, Phosphides of. Cd and P are said to combine when heated together to form a grey, slightly metal-like, mass, which burns in air to phosphates, and dissolves in HClAq with evolution of PH_3 (Stromeyer, *S.* 22, 362). According to B. Renault (*C. R.* 76, 283) when P vapour is passed over hot Cd, two phosphides are formed, Cd_3P_2 and Cd_2P. Oppenheim (*B.* 5, 979) describes Cd_3P_2 as a grey, metal-like, crystalline substance, produced by heating CdO with KOHAq and P, and heating in H.

Cadmium, Salts of. Compounds obtained by replacing the H of acids by Cd. The Cd salts form one series CdX_2, when $X_2 = Cl_2$, $(NO_3)_2$, $(ClO_3)_2$, SO_4, CO_3, HPO_4, &c. The V.D. of one salt, $CdBr_2$, has been determined; from this result, and from the similarities between the salts of Cd and Zn, it is probable that the gaseous molecules of the haloid Cd salts are

correctly represented by the formula CdX_2 where X = F, Cl, Br, or I. The greater number of the salts of Cd are soluble in water; the aqueous solutions redden blue litmus paper; they are poisonous. The haloid salts are not decomposed by heat; salts of volatilisable acids give CdO when strongly heated. Many Cd salts are isomorphous with corresponding salts of Zn; some, especially more complex double salts, are isomorphous with corresponding salts of Mg, Ni, Co, and Zn. A great many double salts containing CdX_2(X = Cl,Br,I) are known; but few basic salts of Cd have been prepared. The principal Cd salts are *borate; bromate; carbonates, &c. chlorate, perchlorate; chromate; cyanates, &c.; iodate, periodate; molybdate; nitrates, nitrites; phosphates, phosphite; selenates, selenite; sulphates, sulphite, &c.; tungstate; vanadate*: v. BORATES, CARBONATES, &c.

Cadmium, Selenide of. CdSe. Golden yellow, metal-like, crystalline, mass; by heating Cd in Se vapour; S.G. 8·79 (Stromeyer, *S.* 22, 362). The same body is said to be formed as a dark-brown pp. by passing H_2Se into solution of a Cd salt (Vigier, *Bl.* 1861. 5; Renault, *C. R.* 76, 283).

Cadmium, Silicofluoride of. $CdSiF_6$. Long, columnar, deliquescent crystals, obtained by action of H_2SiF_6Aq on CdO (Berzelius, *P.* 1, 26).

Cadmium, Sulphide of. CdS. Occurs native in hexagonal prisms ($a:c$ = 1:·81257) as *Greenockite*. Obtained as an amorphous yellow solid, by repeatedly heating to dull redness $CdSO_4$ in H_2S (v. Hauer, *J. pr.* 72, 338); by passing H_2S into a slightly acid solution of a Cd salt; by heating Cd with SO_2Aq (Geitner, *A.* 87, 34; Fordos a. Gélis, *A.* 50, 260; Schweitzer, *C. N.* 23, 293). Obtained also in crystalline form by fusing the amorphous CdS with K_2CO_3 and S (Schüler, *A.* 87, 34); by heating $CdCl_2$ in H_2S; or by melting together $CdSO_4$, CaF_2, and BaS (Troost a. Deville, *C. R.* 52, 920). CdS is also produced in crystals, but in small quantity, by passing S vapour over strongly heated CdO, or Cd (Follenius, *Fr.* 13, 411; Sidot, *C. R.* 62, 999). Crystalline CdS is non-volatile at any temperature; it dissolves easily in boiling conc. HClAq, or dilute H_2SO_4Aq (Follenius, *l.c.*; Hofmann, *A.* 115, 286); S.G. 4·5, when melted 4·6. Schiff (*A.* 115, 74) described CdS_5 as a yellow powder obtained by the action of K_2S_5Aq on a neutral Cd salt in solution; according to Follenius (*Fr.* 13, 411) this yellow solid is a mixture of CdS and S.

Cadmium, Sulphocyanide of. $Cd(CNS)_2$. Obtained by action of HCNSAq on $CdCO_3$; *v.* SULPHOCYANIDES, under CYANIDES.

Cadmium, Telluride of. CdTe. Black crystals, S.G. 6·20, by heating Cd with Te, and subliming the product in H (Margottet, *C. R.* 85, 1142).

M. M. P. M.

CADMIUM ETHIDE $CdEt_2$. Obtained in impure condition from EtI and Cd. Takes fire in air (Wanklyn, *C. J.* 9, 193; Sonnenschein, *J. pr.* 67, 169).

CÆSIUM. Cs. At. w. 132·7. [26°–27°] (Setterberg, *A.* 211, 100). S.G. $\frac{15°}{}$ 1·88 (Setterberg, *l.c.*). S.V.S. 70·7. Discovered by Bunsen and Kirchoff as chloride in the water of a mineral spring at Dürkheim (*P.* 113, 342). Name given because element characterised by two sky-blue (*cæsius*) lines in the spectrum.

Occurrence.—Never free. Salts very widely distributed, but in very small quantities, along with Rb, chiefly as chloride and oxide; in many minerals and mineral waters, in sea water and sea weed, in residues from saltpetre refining, in ash of tobacco, tea, coffee, and oak wood, &c. (*v.* especially Laspeyres, *A.* 134, 349; 138, 326: also Smith, *Am. S.* [2] 49, 335; Erdmann, *J. pr.* 86, 377; Grandeau, *C. R.* 53, 1100; Lonstadt, *C. N.* 22, 25 a. 44). The rare mineral *Pollux*, from Elba, according to analyses by Pisani, contains 34 p.c. Cs oxide combined with silica, and is free from Rb (*A.* 132, 31).

Preparation.—1. The mother liquor, obtained by repeatedly evaporating the water of the mineral spring at Nanheim, and separating from the crystals which form, contains nearly ½ p.c. CsCl. Fe, Al, and the alkaline earth metals, are removed in the usual way; the liquid is evaporated, and heated to volatilise ammonium salts added in the preceding processes; the residue is dissolved in water and the Cs and Rb are ppd. as double chlorides of Cs, or Rb, and Pt, by addition of $PtCl_4Aq$. The pp. is boiled in a *very little* water, and allowed to settle, the water is poured off while still hot; this process is repeated about 20 times, when the pp. will be quite free from K_2PtCl_6 and will consist of Cs_2PtCl_6 mixed with Rb_2PtCl_6. The pp. is now reduced in H, CsCl and RbCl are dissolved out in boiling H_2O (Böttger, *J. pr.* 91, 126). The mixed chlorides are converted into sulphates, these are dissolved in H_2O, BaOAq is added, $BaSO_4$ is removed by filtration, and the filtrate is evaporated to dryness in a silver dish after addition of $(NH_4)_2CO_3$; the residue is dried, dissolved in water, $BaCO_3$ removed by filtration, and twice as much $H_2.C_4H_4O_6$ is added as is required to neutralise the solution of Cs_2CO_3 and Rb_2CO_3; the liquid is evaporated at 100° and crystallised; the pp. consists of $CsH.C_4H_4O_6$ mixed with $RbH.C_4H_4O_6$. As the latter salt requires 8 times as much H_2O as the former for solution, the two salts may be completely separated by fractional precipitation; this process is continued until the crystals of Cs tartrate do not show a trace of Rb in the spectroscope (Bunsen, *P.* 119, 1; Allen, *P. M.* [4] 25, 189). By heating the tartrate, and dissolving the residue in H_2SO_4Aq, and crystallising, Cs_2SO_4 may be prepared; this is dissolved in H_2O, decomposed by BaOAq, and the solution is filtered and evaporated to dryness in a silver dish, when CsOH is obtained. The CsOH is dissolved in absolute alcohol, and dry HCN is passed into this solution: CsCN is thus obtained as a white solid (Setterberg, *A.* 211, 100). A mixture of 4 parts CsCN and 1 part $Ba(CN)_2$ is heated just to melting in a porcelain crucible, and an electric current from 2 or 3 Bunsen cells is passed into the molten mass, in the manner described by Bunsen (*P.* 155, 633). The contents of the crucible are then warmed under petroleum when the metallic Cs melts into globules (Setterberg, *A.* 211, 100).—2. The mixed chlorides of Cs and Rb, obtained as in 1, are converted into sulphates, and then into alums by adding Al_23SO_4Aq and evaporating. Rb alum is 4 times more soluble than Cs alum; Cs alum

may be obtained quite free from Rb by a few crystallisations. The Cs alum is dissolved in hot H_2O, and ppd. by NH_3Aq, the liquid is filtered from Al_2O_3, evaporated to dryness in a Pt dish and strongly heated to remove $(NH_4)_2SO_4$; the residue is dissolved in H_2O, and $BaCl_2Aq$ is added so long as a pp. of $BaSO_4$ forms; the pp. is filtered off, NH_3Aq and $(NH_4)_2CO_3Aq$ are added to the filtrate, the liquid is kept warm for some time, and is then filtered from any $BaCO_3$ which has formed; the filtrate is evaporated to dryness, and heated to fusion; solution in H_2O, treatment with NH_3Aq and $(NH_4)_2CO_3$, evaporation, and fusion are repeated; finally CsCl is obtained by dissolving the fused mass in H_2O, and crystallising (Godeffroy, *A.* 181, 176; Redtenbacher, *J. pr.* 95, 148). This is converted into Cs_2SO_4 and then into CsOH which is treated as described in 1.—3. *Lepidolite* (a silicate of Al), from Hebron, in Maine, U.S.A., contains about ·4 p.c. Cs oxide and ·2 p.c. Rb oxide. The powdered mineral is well mixed with 2 parts freshly slaked CaO, and very strongly heated for some time; the mass is powdered, half its weight of conc. H_2SO_4Aq is added, followed by water; the whole is boiled, filtered, and evaporated to dryness; the residue is dissolved in water, filtered from $CaSO_4$ and evaporated until the alums of K, Cs, and Rb crystallise out. About 4 kilos. of the crude mixed alums was prepared by Setterberg (*A.* 211, 100), and dissolved in hot water, so that the solution had S.G. = 20° Beaumé; this was cooled slowly to 45°, when the Cs and Rb alums were deposited, as they are insoluble in cold conc. potash alum solution. The alums were dissolved in a little hot water and again cooled, and then solution and crystallisation was continued until the crystals were free from potash. Cs alum is 4 times less soluble in H_2O than Rb alum, and is insoluble in a saturated solution of the latter; the mixed alums were dissolved in a little hot water, and allowed to cool, when Cs alum separated with a little Rb alum; this process was repeated until pure Cs alum was obtained. The alum was dissolved in hot water, enough BaOAq added to ppt. Al_2O_3 and all the H_2SO_4, the solution was filtered off and evaporated to dryness: the CsOH thus obtained was dissolved in absolute alcohol, and CsCN was prepared; the CsCN was then electrolysed as described in 1. (For other processes for preparing pure salts of Cs *v.* Godeffroy, *B.* 7, 241; Cossa, *B.* 11, 812; Stolba, *D. P. J.* 197, 336; 198, 225; Sharples, *Am. Ch.* 3, 453. For an account of attempts to prepare the metal by various methods similar to those used for preparing Rb, *v.* Smith, *Am. Ch.* 6, 106.)

Properties.—Silver white, soft, ductile, metal; oxidises rapidly with production of heat and light in air; decomposes H_2O at ordinary temperature with inflammation of H produced. Melts 26°–27°; S.G. at 15° 1·88 (Setterberg, *A.* 211, 100). Spectrum characterised by two lines in the blue, Cs_α = 4560, Cs_β = 4597; ·00005 mgm. Cs may be detected by the spectroscope; ·003 CsCl may be detected in presence of 300-400 parts of KCl or NaCl; ·001 CsCl in presence of 1500 LiCl (Bunsen, *l.c.*). The atomic weight of Cs has been determined (1) by determination of V.D. of CsCl, and analyses of the same salt; by Bunsen (*P.* 113, 353; 119, 4), by Johnson a. Allen (*Am. S.* 35, 94), and by Godeffroy (*A.* 181, 185); (2) by comparing the reactions of Cs compounds with compounds of Li, K, Na, and Rb. One gaseous compound of Cs has been obtained; the S.H. of the metal has not been determined. Cs is positive to all other elements (*v.* ALKALI METALS).

Combinations.—No compounds of Cs have as yet been prepared directly from the metal. When conc. CsClAq is electrolysed with Pt as the +, and Hg as the − electrode, an amalgam of Cs and Hg is formed, and solidifies to a white crystalline mass; the Cs in this amalgam very quickly oxidises to CsOH.

Detection and Estimation.—Most of the salts of Cs are easily soluble in water. Cs salts may be detected by the comparative insolubility in H_2O of Cs_2PtCl_6 (*v. Preparation*, No. 1), and by the spectroscope. There is no satisfactory method for separating and estimating Cs salts; the pp. by $PtCl_4$ contains Rb_2PtCl_6 and a little K_2PtCl_6; by repeating the ppn. the pp. may be obtained almost free from K_2PtCl_6; the pp. is then reduced in H, the CsCl and RbCl dissolved out, the liquid evaporated and the residue weighed; the Cl is then estimated and the quantity of CsCl is calculated.

Cæsium chloride CsCl. Mol. w. 168·07 (Scott, *Pr. E.* 1888). For preparation *v.* CÆSIUM, *Preparation*, No. 2. Small, white, cubes; not deliquescent when pure; partially decomposed by melting in air, residue is alkaline. Melts at low red heat, and volatilises at a higher temperature. Easily soluble in H_2O and alcohol. CsCl forms several double compounds, insoluble in conc. HClAq, with other metallic chlorides; they are obtained by adding CsCl in conc. HClAq to a solution of the other chloride also in conc. HClAq. The following are known: $2CsCl.CdCl_2$, $2CsCl.HgCl_2$, $2CsCl.ZnCl_2$, $2CsCl.CuCl_2$, $2CsCl.MnCl_2$, $2CsCl.NiCl_2$, $2CsCl.PdCl_2$, $6CsCl.Fe_2Cl_6$, $6CsCl.BiCl_3$, $6CsCl.SbCl_3$, $CsCl.AuCl_3$, $2CsCl.PtCl_4$ (Stolba, *D. P. J.* 198, 225; Godeffroy, *B.* 7, 375; 8, 9); $2CsCl.PtCl_4$, S. (0°) ·024, (100°) ·377. When molten CsCl is electrolysed in an atmosphere free from O, a small blue mass is obtained which is dissolved by H_2O with evolution of H; probably this is due to formation of a subchloride.

Cæsium cyanide CsCN. Prepared by the action of dry HCN on CsOH dissolved in absolute alcohol; *v.* CYANIDES.

Cæsium hydroxide CsOH. Mol. w. unknown. Prepared (as described under CÆSIUM, *Preparation*, No. 1) by decomposing Cs_2SO_4Aq by BaOAq, filtering off $BaSO_4$, and evaporating to dryness in a silver dish. Grey-white solid, melting below redness; undecomposed by heat; deliquesces in air, with production of much heat, to form strongly alkaline CsOHAq.

Cæsium oxide. An oxide of Cs has not yet been prepared.

Cæsium, Salts of. Compounds obtained by replacing H of acids by Cs. CsOHAq acts as a very strong base. The salts belong to one series CsX where X = Cl, NO_3, $\frac{SO_4}{2}$, $\frac{CO_3}{2}$ &c.; the formulæ are established from the vapour

density of CsCl, (Scott, *Pr. E.* 1888), and also by comparing the salts with those of the other alkali metals. The salts of Cs are very similar to those of Rb; they are well marked, stable, compounds; no basic salts are known; so far as investigation has gone the Cs salts show a marked tendency to form double salts. Most of the salts of Cs are soluble in water; the solutions are ppd. by $PtCl_4Aq$ (yellow), by $H_2.C_4H_4O_6Aq$ (white), by $HClO_4Aq$ (white), and by silicotungstic acid (white). The chief salts are *carbonates, nitrate, selenates, silicotungstate, sulphates, tartrate* (*v.* CARBONATES, &c.).

M. M. P. M.

CAFFEÏC ACID $C_9H_8O_4$ *i.e.* [4:3:1] $C_6H_3(OH)_2.CH:CH.CO_2H$. *Di-oxy-cinnamic acid. Di-oxy-phenyl-acrylic acid.*

Formation.—1. By boiling caffetannic acid with aqueous KOH (Hlasiwetz, *A.* 142, 221).—2. From its acetyl derivative.—3. Powdered cuprea bark is extracted with ether followed by alcohol; the residue is boiled with aqueous KOH, H_2SO_4 is added, and the liquid filtered while hot. The filtrate, when cold, is exhausted with ether, and the ethereal solution, after decolourising with animal charcoal, is set aside to crystallise (G. Körner, *Ph.* [3] 13, 246).—4. From hemlock (in which it is combined with conhydrine?) (Hofmann, *B.* 17, 1922).

Properties.—Yellow monoclinic tables (containing ½aq), v. e. sol. alcohol. The aqueous solution is turned green by Fe_2Cl_6, on adding Na_2CO_3 it then changes to blue and violet. It does not reduce Fehling's solution but reduces warm ammoniacal $AgNO_3$. Its solution in KOHAq turns brown in air.

Reactions.—1. *Dry distillation* gives pyrocatechin.—2. *Potash fusion* forms protocatechuic acid.—3. *Sodium amalgam* reduces it to di-oxy-phenyl-propionic acid.

Salts.—CaA'_2 3aq.—SrA'_2 4aq.—BaA'_2 4aq. $Ba_3(C_9H_5O_4)_2$ 9aq.—$Pb_3(C_9H_5O_4)_2$ 2aq.

Mono-methyl derivative v. FERULIC ACID.

Di-methyl derivative $C_6H_3(OMe)_2.CH:CH.CO_2H$. [180°]. Formed by saponifying the ether or by heating caffeïc or ferulic acid with MeI and KOH. White needles. Sol. alcohol and ether, nearly insol. water. On oxidation with $KMnO_4$ it produces veratric acid. Methyl ether A'Me. [64°]. Prisms. Prepared by methylation of isoferulic acid (Tiemann a. Will, *B.* 11, 651; 14, 959).

Methylene ether $CH_2{<}^{O}_{O}{>}C_6H_3.CH:CH.CO_2H$. [232°]. Formed by boiling piperonal $CH_2O_2:C_6H_3.CHO$ with NaOAc and Ac_2O (Lorenz, *B.* 13, 757). Minute crystals (from dilute alcohol). Conc. H_2SO_4 forms a brick-red solution.—AgA'.

Acetyl-methyl derivative v. ACETYL-FERULIC ACID.

Di-acetyl derivative $C_6H_3(OAc)_2CH:CH.CO_2H$. [191°]. From caffeïc acid and Ac_2O or by heating protocatechuic aldehyde (2 pts.) with NaOAc (2 pts.) and Ac_2O (6 pts.). Slender needles. V. sl. sol. water, v. sol. alcohol and ether (Tiemann a. Nagai, *B.* 11, 659).

Hydro-caffeïc acid *v.* DI-OXY-PHENYL-PROPIONIC ACID.

CAFFEÏDINE $C_7H_{12}N_4O$. Formed, together with methylamine, CO_2, and NH_3, by boiling caffeïne with conc. baryta-water (Strecker, *A.* 123, 360; 157, 1; *C. R.* 52, 1269; Schmidt, *B.* 14, 816; Schultzen, *Z.* 1867, 616). Alkaline liquid. Sol. water, alcohol, and chloroform, sl. sol. ether. Long boiling with baryta-water gives methyl-amido-acetic acid, formic acid, CO_2, and NH_3. Chromic acid oxidises it to di-methyl-oxamide, methylamine, CO_2, and NH_3 (Maly a. Andreasch, *M.* 4, 381). EtI forms $C_7H_{11}EtN_4O$.

Salts.—B'HCl.—$B'_2H_2PtCl_6$ 4aq.

CAFFEÏDINE CARBOXYLIC ACID $C_8H_{12}N_4O_2$. Prepared by the gradual solution of caffeïne in dilute NaOHAq; this solution is neutralised with HOAc and the copper salt ppd. with $Cu(OAc)_2$ (Maly a. Andreasch, *M.* 4, 369). Very soluble crystalline mass; its aqueous solution on boiling gives off CO_2 and leaves caffeïdine.

Salts.—KA': golden syrup. $HgA'_2 2HgCl_2$: bulky pp.—CuA'_2: minute crystalline granules.—CaA'_2.—ZnA'_2.—CdA'_2.—MgA'_2.

CAFFEÏNE $C_8H_{10}N_4O_2$. *Theïne.* [230·5°]. S.G. $\frac{19}{}$ 1·23. S. 1·35 at 16°; 45·6 at 65° (Commaille, *C. R.* 81, 817). S. (alcohol) ·61 at 16°; 3·12 at 78°. S. (ether) ·044 at 16°. S. (CS_2) ·06 at 16°. S. (chloroform) 13 at 16°.

Occurrence.—1. In coffee berries and leaves (Runge, *Materialien zur Phytologie*, 1820; Stenhouse, *P. M.* [4] 7, 21; Pfaff a. Liebig, *A.* 1, 17). Coffee berries contain from 1 to 1·28 p.c. caffeïne; roasted coffee about 1·3 p.c. (Paul a. Cownley, *Ph.* [3] 17, 565; *cf.* Stenhouse a. Campbell, *C. J.* 9, 33; *A.* 89, 246).—2. In tea leaves (Oudry, *Mag. Pharm.* 19, 49; Jobst, *A.* 25, 63; Mulder, *P.* 43, 160). Tea contains 2 to 4 p.c.—3. In guarana, the dried pulp of *Paullinia sorbilis* (Martius, *A.* 36, 93). Guarana contains about 5 p.c. of caffeïne.—4. In Maté or Paraguay tea the leaves and twigs of Ilex Paraguayensis (Stenhouse, *P. M.* [3] 23, 426). 5. In the seeds of the Kola tree (*Cola acuminata*) of West Central Africa, to the amount of 2·13 p.c. of the dried seed (Attfield, *Ph.* [2] 6, 457).—6. Present to a small extent in cocoa (E. Schmidt, *A.* 217, 306).

Formation. By heating silver theobromine with MeI for 20 hours at 100°: caffeïne is thus shown to be methyl-theobromine (Strecker, *A.* 118, 151; E. Schmidt, *A.* 217, 282).

Preparation.—1. Tea or coffee is exhausted with boiling water; tannin is ppd. by lead subacetate; the filtrate is freed from lead by H_2S and evaporated to crystallisation (Péligot, *A. Ch.* [3] 11, 129).—2. Raw ground coffee (5 pts.) is mixed with moist lime (2 pts.) and extracted with alcohol, chloroform, or benzene, from which the caffeïne crystallises on evaporation (Versmann, *Ar. Ph.* [2] 68, 148; Vogel, *C. C.* 1858, 367; Payen *A. Ch.* [3] 26, 108; Paul a. Cownley, *Ph.* [3] 17, 565).—3. Tea or coffee is boiled with water and either the whole, or else the filtrate, is evaporated to a syrup, mixed with slaked lime and extracted with chloroform (Aubert, *Pflüger's Archiv*, 5, 589; Cazeneuve a. Caillol, *Bl.* [2] 27, 199).—4. By sublimation from tea (Heijnsius, *J. pr.* 49, 317).—5. A decoction of tea is evaporated with PbO to a syrup, K_2CO_3 is added, and caffeïne extracted by alcohol (Grosschoff, *J.* 1866, 470).

Properties.—Mass of slender silky needles (containing aq); begins to sublime at 79°

(Blyth). Sl. sol. cold water and alcohol, v. sl. sol. ether. The crystals from alcohol and ether are anhydrous. Weak base; the salts being decomposed by water; does not affect red litmus. Tastes bitter. Produces tetanus and rigor in the voluntary muscles of frogs (Aubert; Brunton a. Cash, *Pr.* 42, 238). In men it increases the heart's action, excites the nervous system, and diminishes metabolism (?) (Lehmann, *A.* 87, 205). Caffeïne gives a yellow pp. with phosphomolybdic acid.

Estimation.—The various methods of preparation may also be used for estimation (Stenhouse, *A.* 102, 126; Lieventhal, *C. C.* 1872, 631; Weyrick. *Fr.* 12, 141; Péligot, *Rep. Pharm.* 82, 340; Claus, *J.* 1863, 708, Zöller, *J.* 1871, 818; Mulder, *J. pr.* 15, 280; Commaille, *Bl.* [2] 25, 261; Paul a. Cownley, *Ph.* [3] 17, 565).

Colour Test.—Evaporate with chlorine-water on platinum-foil. A yellowish residue is left, which on further heating becomes red, and is turned purple by ammonia (Schwarzenbach, *J.* 1861, 871; 1865, 730). Xanthine, theobromine and uric acid also give this test. Caffeïne evaporated with conc. HNO_3 gives a yellow residue (amalic acid) which is also turned purple (murexide) by ammonia (Rochleder, *A.* 69, 120).

Reactions.—1. Gaseous *chlorine* or HCl and $KClO_3$ give in the first place di-methyl-alloxan and methyl-urea (E. Fischer, *A.* 215, 257):
$C_8H_{10}N_4O_2 + O_2 + 2H_2O = C_6H_8N_2O_5 + C_2H_6N_2O$.
Part of the di-methyl-alloxan becomes amalic acid. Chloro-caffeïne, methylamine, and cyanogen chloride are also formed, and, if the reaction is prolonged, di-methyl-parabanic acid (cholestrophane). *Bromine* and water at 100° act similarly (Maly a. Hinterberger, *M.* 3, 85).—2. Cold HNO_3 attacks it slowly, giving off CO_2 (1 vol.) and N_2O (about 2 vols.) (Franchimont, *R. T. C.* 6, 223).—3. Hot dilute HNO_3 gives di-methyl-parabanic acid (Stenhouse, *A.* 45, 366; 46, 227; Rochleder, *A.* 69, 120; 71, 1).—3. *Chromic acid* gives di methyl-parabanic acid, NH_3, methylamine, and CO_2 (Maly a. Hinterberger, *M.* 2, 87).—4. Boiling *baryta water* splits up caffeïne into caffeïdine and CO_2; the caffeïdine then breaks up into CO_2, NH_3, methylamine, formic acid, and methyl-amido-acetic acid (sarcosine) (Rosengarten a. Strecker, *A.* 157, 1). 5. With conc. HCl at 250° it forms ammonia, methylamine, sarcosine, formic acid and CO_2 (E. Schmidt, *A.* 217, 270). The volume of NH_3 is to that of $NMeH_2$ as 1:2 Below 200°, HCl has no action. Hence there are three NMe groups in caffeïne, $C_8H_{10}N_4O_2 + 6H_2O = 2CO_2 + 2NMeH_2 + NH_3 + CH_2O_2 + C_3H_7NO_2$.

Salts.—(E. Schmidt, *A.* 217, 282; Herzog, *A.* 26, 344; 29, 171; Biedermann, *Ar. Ph.* [3] 21, 175; Tilden, *C. J.* 18, 99; 19, 145.) B′HCl.—B′HCl 2aq: monoclinic; decomposed by moist air into HCl and caffeïne.—B′2HCl.—B′4HCl.—$B'_2H_2PtCl_6$ (at 100°).—$B'HAuCl_4$ 2aq: glittering plates.—B′HBr 2aq.—B′HI.—B′2HI.—$B'HI_3$ $1\frac{1}{2}$aq (Tilden). — B′HClCl: [175°]; yellow needles converted by NH_3 into a greenish-black pp. (Tilden, *Z.* 1866, 350; Ostermayer, *B.* 18, 2298).—$B'HNO_3$aq.—$B'H_2SO_4$.—$B'H_2SO_4$aq.

Formate $B'H_2CO_2$.—**Acetate** B′2HOAc.—**Butyrate** $B'C_4H_8O_2$.—**Isovalerate** $B'C_5H_{10}O_2$.—**Citrate**: prepared by adding a solution of citric acid (1 pt.) in alcohol ($7\frac{1}{2}$ pts.) to one of caffeïne (1 pt.) in chloroform ($14\frac{1}{2}$ pts.) and evaporating. Semi-crystalline powder, decomposed by most solvents (Lloyd, *Ph.* [3] 11, 760). According to Tanret (*J. Ph.* [5] 5, 591) the last five salts are merely mixtures. — **Caffeate** $B'C_9H_8O_4$ 2aq (Hlasiwetz, *A.* 142, 226).

Combinations.—$B'HgCl_2$ (Nicholson, *A.* 62, 78; Hinterberger, *A.* 82, 316).—$B'HgCy_2$ (Kohl a. Swoboda, *A.* 83, 341).—$B'AgNO_3$.

Methylo-chloride B′MeCl aq. At 200° it splits up into MeCl and caffeïne.—$(B'MeCl)_2PtCl_4$. Sparingly soluble.

Methylo-iodide B′MeI aq (Tilden, *J. pr.* 94, 374; E. Schmidt, *A.* 217, 286; E. Schmitt a. E. Schilling, *A.* 228, 141). From caffeïne and MeI at 130°. At 100° it loses aq, at 190° it splits up into caffeïne and MeI. Triclinic: $a:b:c = \cdot6962:1:\cdot4161$; $\alpha = 91°24'$; $\beta = 74°$; $\gamma = 88°$.—$B'MeI_3$.

Methylo-hydroxide B′MeOHaq [91°], and B′MeOH [138°]. From the methyloiodide and Ag_2O (Schmitt a. Schilling, *A.* 228, 143). Crystals. V. sol. water, alcohol, and chloroform. v. sl. sol. ether or light petroleum. Its solutions are neutral. It is not poisonous. Heated at 200° in the dry state it gives off methylamine while caffeïne is also formed. HCl or dilute H_2SO_4 convert only part of it into the corresponding salt, the rest gives methylamine, formic acid and dimethyldialuric acid, the latter being converted by atmospheric oxygen into amalic acid. When HCl is used, caffeïne methylochloride is one of the products. With water at 200° it gives sarcosine, methylamine, formic acid, and CO_2. Chromic acid forms cholestrophane, methylamine, formic acid and CO_2.

Ethylo-triiodide $B'EtI_3$. From caffeïne and EtI at 130° (Tilden, *C. J.* 18, 99; 19, 145).—$B'_2Et_2PtCl_6$.

Chloro-caffeïne $C_8H_9ClN_4O_2$. [188°]. Formed by passing chlorine into dry caffeïne in dry $CHCl_3$. Crystallised from water. V. sl. sol. cold water and ether, v. sol. strong acids but ppd. by water. Reduced to caffeïne by zinc-dust and HCl (Fischer, *A.* 215, 262; 221, 336).

Bromo-caffeïne *v.* p. 561.

Amido-caffeïne $C_8H_9(NH_2)N_4O_2$. [above 360°]. From bromo-caffeïne (2 pts.) and alcoholic NH_3 (20 pts.) by heating for 7 hours at 130° (Fischer, *A.* 215, 265). Slender needles; may be distilled. V. sl. sol. water and alcohol; sol. conc. HOAc; sol. conc. HClAq, but reppd. by water, being apparently less basic than caffeïne.

Oxy-caffeïne $C_8H_9(OH)N_4O_2$. [c. 345°]. From ethoxy-caffeïne by heating with dilute HCl (Fischer, *A.* 215, 268). Mass of white needles (from water). V. sl. sol. alcohol, ether, or cold water. Sol. conc. HCl but reppd. by water. Oxy-caffeïne is an acid.—NaA′ 3aq. Needles.—BaA'_2 3aq. *Reactions.*—1. The silver salt with EtI at 100° gives ethoxy-caffeïne.—2. PCl_5 in $POCl_3$ gives chloro-caffeïne.—3. Cl at a high temperature gives di-methyl-alloxan.—4. Cl gas at 0° in a solution of oxy-caffeïne in HCl gives apo- and hypo-caffeïne.—5. Dry *bromine* forms an addition compound $C_8H_9(OH)N_4O_2Br_2$(?) as a red mass, decomposed by water or alcohol, the latter giving diethoxy-oxy-caffeïne dihydride.

Ethoxy-caffeïne $C_8H_9(OEt)N_4O_2$. [140°]. From bromo-caffeïne and alcoholic KOH (Fis-

cher, *A.* **215**, 266). White needles (from water). Sl. sol. cold alcohol or ether, v. e. sol. hot alcohol. Melts in boiling water, partly dissolving. Sol. dilute HCl and reppd. by KOH.

Di-methoxy-oxy-caffeïne dihydride $C_8H_8N_4O_2(OMe)_2OH$. [179°]. Prepared by the action of methyl alcohol on oxy-caffeïne bromide. Colourless crystals. Sol. water and alcohol. By HCl it is decomposed into methyl alcohol, methylamine and apo-caffeïne (Fischer, *B.* 14, 642).

Di-ethoxy-oxy-caffeïne dihydride $C_8H_9(OEt)_2(OH)N_4O_2$ *Di-ethyl derivative of tri-oxy-caffeïne dihydride.* [195°–205°]. From oxy-caffeïne, Br, and alcohol, as above. Warmed with HCl it gives alcohol, methylamine, apo-caffeïne, and hypo-caffeïne. Fuming HI or HI gas passed into chloroform solution reduces it to oxy-caffeïne. With *phosphorus oxychloride* it forms a crystalline substance that appears to be $C_8H_8N_4O_2(OH)(OEt)Cl$. This body is reconverted by alcohol into diethoxy-oxy-caffeïne dihydride, but it is decomposed by water, one of the products being di-methyl-alloxan, although this is not formed from diethoxy-oxy-caffeïne dihydride by water or acids (Fischer a. Reese, *A.* **221**, 337).

Allo-caffeïne $C_8H_9N_3O_5$. [198°]. A by-product obtained in the preparation of the preceding body from oxy-caffeïne, bromine and alcohol, especially when the latter is wet (92 p.c.). Sandy powder. V. sl. sol. water, sl. sol. boiling alcohol. Decomposed by boiling HCl (Fischer, *A.* 215, 276).

Apo-caffeïne $C_7H_7N_3O_5$. [148°].

Formation.—1. From di-ethoxy-oxy-caffeïne dihydride (5 g.) by evaporating with (20 g.) dilute (20 p.c.) HCl at 100° (Fischer, *A.* 215, 277); the equation is: $C_8H_9(OH)N_4O_2(OEt)_2 + 2H_2O = C_7H_7N_3O_5 + MeNH_2 + 2HOEt$. –2. From oxy-caffeïne and aqueous Cl at −10°. –3. From caffeïne, HCl and $KClO_3$ (Maly a. Andreasch *M.* 3, 100).

Properties. — Monoclinic crystals (from water). $a:b:c = \cdot8025:1:\cdot6976$. V. sol. hot water, alcohol or chloroform, sl. sol. cold water, benzene or CS_2. Boiling water decomposes it into CO_2, hypo-caffeïne and caffuric acid (*q. v.*).

Hypo-caffeïne $C_6H_7N_3O_3$. [182°].

Formation. — 1. Formed along with apo-caffeïne by warming the di-ethyl derivative of tri-oxy-caffeïne dihydride with hydrochloric acid, thus: $C_8H_9(OH)N_4O_2(OEt)_2 + 2H_2O = C_6H_7N_3O_3 + 2HOEt + NH_2Me + CO_2$. — 2. From oxy-caffeïne, HCl and Cl (Fischer, *A.* 215, 288).

Properties. — Crystallised from water. V. sol. hot water or alcohol, sl. sol. cold water. May be distilled with but slight decomposition. $Ba(C_6H_6N_3O_3)_2C_6H_7N_3O_3$: v. sol. water.

Reactions.—Not affected by boiling fuming HNO_3, chlorine- or bromine-water, $K_2Cr_2O_7$ and dilute H_2SO_4, $HMnO_4$, conc. HCl, fuming HI, Sn and HCl, Ac_2O or $POCl_3$ and PCl_5. Water at 150° completely destroys it. Boiled with baryta it gives caffolin (*q. v.*).

Caffolin $C_5H_9N_3O_2$. [194°–196°]. Formed by boiling hypo-caffeïne with lead sub-acetate (Fischer, *A.* 215, 292). Slender needles (from alcohol) or long prisms (from warm water). V. e. sol. warm water. Sl. sol. alcohol. Does not combine with acids. It is but a feeble acid, for its barium compound is decomposed by CO_2. Boiled with Ag_2O, it forms a crystalline silver compound.

Reactions.—1. Conc. HCl at 100° splits it up into CO_2, NH_3, $NMeH_2$ &c.—2. Conc. HI forms methyl-urea.—3. K_3FeCy_6 gives methyl-oxamic acid and methyl-urea: $C_5H_9N_3O_2 + O + H_2O = MeNH.CO.CO_2H + MeNH.CO.NH_2$. — 4. $KMnO_4$ and KOH give di-methyl-oxamide and ammonia according to the reaction: $C_5H_9N_3O_2 + O + H_2O = MeNH.CO.CO.NHMe + CO_2 + NH_3$.—5. Potassium bichromate and H_2SO_4 give cholestrophane: $C_5H_9N_3O_2 + O = C_5H_6N_2O_3 + NH_3$. — 6. *Nitrous acid* completely destroys it.—7. Boiled with Ac_2O it forms the acetyl derivative of acecaffin $C_6H_{10}AcN_3O_2$.

Acecaffin $C_6H_{11}N_3O_2$. [110°–112°]. From its acetyl derivative by evaporating with fuming HCl at 100° and decomposing the resulting hydrochloride by Ag_2O (Fischer, *A.* 215, 300). Trimetric crystals (from benzene). $a:b:c = \cdot6707:1:1\cdot2445$. May be distilled undecomposed. V. e. sol. water and alcohol.

Acetyl derivative $C_6H_{10}AcN_3O_2$. [106°–107°]. From caffolin by boiling with Ac_2O as long as CO_2 comes off (12 hours). Monoclinic tables (from chloroform mixed with ether).

Caffuric acid $C_6H_9N_3O_4$. [210°–220°]. From apo-caffeïne by boiling water (Fischer, *A.* 215, 280). $C_7H_7N_3O_5 + H_2O = C_6H_9N_3O_4 + CO_2$. Transparent tables (from alcohol). V. sol. water, sl. sol. cold alcohol, chloroform or ether. Feeble acid, its barium salt being decomposed by CO_2.

Salt.—AgA′. Tables, sl. sol. water.

Reactions.—1. Not affected by *chlorine-* or *bromine-water.*—2. HI converts it into hydro-caffuric acid.—3. Warmed with *lead sub-acetate* it gives mesoxalic acid, methyl-urea and methylamine.—4. Hot KOH gives off NH_2Me.

Hydro-caffuric acid $C_6H_9N_3O_3$. [210°–248°]. From caffuric acid, fuming HI and PH_4I (Fischer, *A.* 215, 285). Colourless prisms (from water). V. sol. hot water, sl. sol. cold water.

Reactions.—1. Gives no pp. when boiled with *lead sub-acetate* (unlike caffuric acid).—2. Gives with ammoniacal $AgNO_3$ a mirror in the cold.—4. *Chlorine-water* oxidises it to caffuric acid.—3. Hot KOH gives off methylamine.—5. Warmed with *baryta* it forms methylamine and methyl-hydantoïn carboxylic acid, the latter splitting up into CO_2 and methyl-hydantoïn.

Methyl-caffuric acid $C_7H_{11}N_3O_4$. [167°]. From allocaffeïne by boiling with water (Schmidt a. Schilling, *A.* 228, 172). Needles (from water). V. sol. water, alcohol and chloroform. Basic lead acetate converts it into mesoxalic acid, methylamine and dimethyl urea.

Amalic acid *v.* p. 149.

Constitution of Caffeïne.—Medicus (*A.* 175, 250) proposed the formula

```
MeN – CO
 |     |
 CO   C––NMe
 |    ||    >CH
MeN – C –– N
```

while Emil Fischer (*A.* 215, 314) proposed

```
Me.N—CH
 |    ||
 CO   C.NCH3
 |    |    >CO
Me.N—C = N
```

. Both formulæ readily re-

present the formation by oxidation of di-methyl-alloxan and methyl urea. According to Fischer's formula the derivatives of caffeïne would be represented as follows: Oxy-caffeïne would be

```
   NMe—C(OH)=C—NMe
CO<         |      >CO.
   NMe——————C=N
```

Ethoxy-oxy-caffeïne dihydride would be

```
   NMe—C(OH)(OEt)—C(OEt).NMe
CO<                |        >CO.
   NMe—————————————C————N
```

Apo-caffeïne would be

```
      O ——C(CO₂H)—NMe
CO<        \       >CO.
      NMe — C——————N
```

Caffuric acid would be

```
    HO.C(CO₂H)—NMe
        \        >CO
   HNMe—C————N
```

Hydro-caffuric acid might be written:

```
    HC(CO₂H)—NMe
      \        >CO.
  HMeN—C ——— N
```

Methyl-hydantoïn carboxylic acid would be

```
  HC(CO₂H) . NMe
  |           >CO;
  CO————————NH
```

whence methyl-hydantoïn

```
  H₂C.NMe
  |      >CO.
  CO.NH
```

Hypo-caffeïne may be

```
    O—CH — NMe
CO<    \      >CO,
    NMe—C=N
```

so that apo-caffeïne would be its carboxylic acid. Caffolin may then be

```
  HO.CH.NMe
  |        >CO;
  HNMeC=N
```

but the formation of cholestrophane

```
     CO — NMe
CO<        |
     NMe—CO
```

from it is in that case somewhat anomalous.

Strecker's caffeïdine (from caffeïne by alkalis) would be

```
  MeHN.CH=C—NMe
          |    >CO
  MeHNC=N
```

which by boiling alkalis gives CO_2, NH_3, $2NMeH_2$, formic acid and sarcosine.

Theobromine will be

```
MeN— CH
 |    ||
 CO   C . NMe
 |    |      >CO
 HN  —C=N
```

not

```
 HN—CH
 |   ||
 CO  C—NMe
 |   |    >CO
 MeN—C=N
```

as is shown by the formation of hypo-ethyl-theobromine.

Somewhat similar formulæ are arrived at if we start from the formula of Medicus. Inasmuch as caffeïn methylo-hydroxide differs from caffeïne in giving no NH_3 but only $NMeH_2$ in its decompositions, we must assume that it has the formula

```
MeN—CO
 |   |
 CO  C—NMe———
 |   ||       >CH
MeN—C—NMe(OH)
```

or

```
MeN—CH
 |   ||
 CO  C—NMe———
 |   |        >CO
MeN—C—NMe(OH)
```

Its decomposition-product, di-methyl-dialuric acid, should, according to Maly a. Hinterberger (*M.* 3, 85), be represented by the formula

```
MeN—CO
 |   |
 CO  CH(OH),
 |   |
MeN—CO
```

which agrees better with the formula of Medicus. On the other hand, the frequent occurrence of methyl-urea as well as s-di-methyl urea among the decomposition-products of caffeïne and its derivatives accords best with Fischer's formula (Schmidt a. Schilling, *A.* 228, 174).

CAFFEOL $C_8H_{10}O_2$. (196°). Given off (to the extent of ·05 p.c.) on roasting coffee together with caffeïne (·18 p.c.), palmitic acid, acetic acid, CO_2, and traces pyrrol, methylamine, and hydroquinone. It is extracted by ether from the liquid distillate (Bernheimer, *M.* 1, 459). Liquid, smelling like coffee, sl. sol. hot water, v. e. sol. alcohol and ether; v. sl. sol. conc. KOHAq. Fe_2Cl_6 colours its alcoholic solution red. Potash-fusion gives salicylic acid. It is perhaps a methyl derivative of *o*-oxy-benzyl alcohol.

CAFFETANNIC ACID $C_{15}H_{18}O_8$. Occurs in coffee berries to the amount of 3 to 5 p.c. as Ca and Mg salt, and perhaps also as a double salt of K and caffeïne (Pfaff, (1830) *Schw.* 61, 487; Rochleder, *A.* 59, 300; 63, 193; 66, 35; 82, 196; Liebich, *A.* 71, 57; Payen, *A. Ch.* [3] 26, 108). Prepared by mixing an alcoholic infusion of coffee with water; filtering from ppd. fatty matter; boiling the filtrate, and ppg. as lead salt by $Pb(OAc)_2$. Colourless mammellated crystalline groups, v. sol. water, m. sol. alcohol; has an astringent taste; strongly reddens litmus. Fe_2Cl_6 colours its solutions green. It does not ppt. ferrous salts, tartar-emetic, or gelatin, but it ppts. quinine and cinchonine. It reduces $AgNO_3Aq$, forming a mirror. Its salts turn green in air. Potash-fusion gives protocatechuic acid. Boiling conc. KOHAq splits it up into caffeïc acid and a sugar (Hlasiwetz, *A.* 142, 220).

S a l t s.—BaA'_2 (at 100°): amorphous, v. sol. water; addition of baryta forms a yellow pp.—$PbC_{15}H_{16}O_8$.—$Pb_3(C_{15}H_{15}O_8)_2$.—$Pb_2C_{15}H_{14}O_8$ (at 100°).

Viridic acid. An acid formed by the atmospheric oxidation of an ammoniacal solution of caffetannic acid. According to Rochleder the green colour of coffee berries is due to calcium viridate. It is ppd. by $Pb(OAc)_2$. Amorphous brown mass, v. sol. water. Conc. H_2SO_4 forms a crimson solution whence water gives a flocculent blue pp. The aqueous solutions are turned green by alkalis, and give a bluish-green pp. with baryta-water (*cf.* Vlaanderen a. Mulder, *J.* 1858, 261).

CAFFOLIN *v.* CAFFEÏNE.

CAFFURIC ACID *v.* CAFFEÏNE.

CAÏL-CEDRIN. A bitter, neutral, resinous substance present to a minute extent in the bark of the *Caïl-cedra* (Caventou, *J. Ph.* [3] 16, 355; 33, 123).

CAÏNCIN $C_{40}H_{64}O_{18}$. *Caïncic acid.* S. ·14. Found in Cainca root (from *Chiococca anguifuga* and *racemosa*) (François, Pelletier, a. Caventou, *J. Ph.* 16, 465; Liebig, *A. Ch.* [2] 47, 185; Rochleder a. Hlasiwetz, *A.* 76, 338; Rochleder, *J. pr.* 85, 275). The root is exhausted with alcohol and the caïncin ppd. either by milk of lime or $Pb(OAc)_2$. Crystalline flakes, tasteless at first, afterwards very bitter; v. sl. sol. water and ether, v. sol. alcohol; reddens litmus. Boiling alcoholic HCl splits it up into a sugar ($C_6H_{12}O_6$) and crystalline caïncetin $C_{22}H_{34}O_4$. Caïncetin is resolved by potash-fusion into butyric acid and caïncigenin $C_{14}H_{24}O_2$ which is possibly related to æscigenin. Caïncin in dilute alcoholic solution is converted by sodium-amalgam into crystalline $C_{36}H_{58}O_{15}$ whence fuming HCl forms gelatinous $C_{18}H_{28}O_2$.

CAJEPUT, OIL OF. A light green oil prepared in India by distilling the leaves of *Melaleuca leucodendron* with water. Its chief constituent is cineol $C_{10}H_{18}O$ (*q. v.*), which is also called cajeputol. P_2O_5 converts it into terpenes (*q. v.*) which when so obtained may be called cajeputenes (Schmidt, *C. J.* 14, 63; Wright a. Lambert, *C. J.* 27, 619; Histed, *Ph.* [3] 2, 804; Blanchet, *A.* 7, 161; Gladstone, *C. J.* 49, 621).

CALAMUS ROOT. According to Geuther (*A.* 240, 92) the acorin prepared by Thoms (p. 60) from *Acorus calamus* is not a definite substance, but is separated by alkalis into a neutral amorphous brown mass ($C_{40}H_{67}NO_7$?) and an acid ($C_{11}H_{18}O_3$?). Calamus root after extraction with water still contains a combined acid ($C_{11}H_{18}O_4$?) which may be extracted by adding HCl and shaking with ether. When the root is distilled with steam, methyl alcohol and a mixture of terpenes (*q. v.*) and a compound $C_{10}H_{16}O$(?) is obtained (G.; Schnedermann, *A.* 41, 374; Kurbatow, *B.* 6, 1210; Gladstone, *C. J.* 17, 1).

CALCIUM. Ca. At.w. 39·91. Mol.w. unknown. Melts at red heat. S.G. 1·57 (Matthiessen, *A.* 93, 27). S.H. (0°–100°) ·1686 (Bunsen, *P.* 141, 1). S.V.S. abt. 25. E.C. (Hg at 0° = 1) 12·5 (Matthiessen, *P. M.* [4] 12, 199; 13, 81). Chief lines in emission-spectrum, 6121·2, 5587·6, 4226·3, 3968, 3932·8.

Occurrence.—Never free. Very widely distributed, and often in large quantities, as silicate, phosphate, sulphate, carbonate, fluoride, &c. Most natural waters contain Ca salts; phosphate and carbonate of Ca are found in plants and animals. Ca salts occur in the sun, fixed stars, and meteorites. Calcium carbonate and burnt lime have been known from very ancient times. In 1722 Fr. Hoffmann showed that lime is a distinct earth; Black (1755) was the first to make a quantitative examination of limestone and burnt lime. In 1808 Davy obtained calcium (impure) by the electrolysis of lime.

Formation.—1. Dry CaI_2 is heated with Na in an iron crucible with an air-tight cover (Liés-Bodart a. Jobin, *A. Ch.* [3] 54, 363; Dumas, *C. R.* 47, 575; Sonstadt, *C. N.* 9, 140).—2. Dry fused $CaCl_2$ (300 parts), Na (100 parts), and pure distilled granulated Zn (400 parts), are heated in a crucible with loosely fitting lid, as high a temperature being maintained as is possible without volatilisation of much Zn; an alloy of Ca and Zn is thus produced ($Zn_{12}Ca$ according to v. Rath, *P.* 136, 434). This alloy is heated in a crucible of gas coke until the Zn is all distilled off (Caron, *C. R.* 48, 450; 50, 547).—3. A boiling conc. solution of $CaCl_2$ is electrolysed, using an amalgamated Pt wire as negative electrode (Bunsen, *A.* 92, 248).

Preparation.—A mixture of dry $CaCl_2$ and $SrCl_2$, in the ratio $2CaCl_2:SrCl_2$, mixed with a little NH_4Cl, is melted in an open crucible; the current from 3 or 4 Bunsen cells is passed through the molten mass, the positive electrode being a stick of carbon, and the negative an iron wire as thick as a knitting needle, drawn out to a fine point. The point of the iron wire is kept just under the surface of the molten mass for a minute or so at a time; the Ca separates in small lumps (Matthiessen, *A.* 93, 277; 94, 108). Frey obtained lumps of Ca weighing from 2½ to 4 grams (*A.* 183, 367); he passed the negative electrode through the stem of a tobacco pipe with the bowl dipping under the molten mass in the crucible; H was then passed into the pipe; when the pipe and bowl were filled with this gas, the H was stopped, and the current was started; the Ca rose into the bowl of the pipe, and being in contact with H remained quite unoxidised.

Properties.—Lustrous, clear yellowish-white, very ductile, but brittle when hammered out, malleable; about as hard as calcspar. Frey (*A.* 183, 367) says it is brittle and cannot be hammered out or drawn into wire. Melts at full red heat, and then burns with yellow flame and production of much heat and light; [Ca, O] = 130,930 (*Th.* 3, 251). Does not oxidise in dry air; but in ordinary air is quickly covered with CaO. Not volatilised at temperature of inflammation (Caron, *C. R.* 48, 440). Decomposes cold H_2O rapidly;

$[Ca, Aq] - [Ca, O^2, H^2, Aq] - 2[H^2, O] = 80,900$

(*Th.* 3. 251). As no compound of Ca has been gasified, the value to be given to the atomic weight of the metal is decided partly by the S.H. and partly by purely chemical considerations. The mass of Ca that combines with 15·96 (*i.e.* with 1 atom) O is 39·91, hence the simplest formula for the oxide is CaO (Ca = 39·91); the same mass of Ca combines with 2 × 35·37 Cl, 2 × 79·75 Br, &c.; the simplest formulæ for the chloride and bromide are therefore $CaCl_2$ and $CaBr_2$ respectively (Ca = 39·91). These formulæ are in keeping with the reactions of the compounds, hence they are adopted. The chief compounds of Ca by analyses of which the value Ca = 39·91 has been found are: (1) $CaCl_2$ (Berzelius, *G. A.* 57, 451; Dumas, *A. Ch.* [3] 55, 190); (2) $CaCO_3$ converted into CaO (Dumas, *C. R.* 14, 537; Erdmann a. Marchand, *J. pr.* 26, 472). Ca is a strongly positive metal, forming well-marked and stable salts by replacing the H of acids. Salts of Ca derived from almost every acid are known; several of these form double salts; very few basic salts are known. CaO_2H_2 is an alkaline hydroxide; CaO combines with H_2O with production of much heat; CaO_2H_2 is dehydrated to CaO at a high temperature. $[CaO, H^2O] = 15,540$ (*Th.* 3, 251). The heat of neutralisation of CaO_2H_2Aq is the same as that of KOHAq,

$NaOHAq$, and BaO_2H_2Aq, viz. 31,150 for H_2SO_4Aq and 27,640 for H_2Cl_2Aq. Ca combines with the halogens with production of heat; $[Ca,X^2] = 169,820$ when X = Cl; 140,850 when X = Br; 107,250 when X = I (*Th.* 3, 251).

Reactions and Combinations.—1. With *water* forms CaOAq and H.—2. With *acids* forms salts, usually evolving H; conc. HNO_3Aq only acts at high temperatures.—3. Combines directly, when heated, with many *non-metals*; especially Cl, Br, I, O, S, P (*v.* CALCIUM CHLORIDE, &c.).—4. Forms *alloys* with several metals, by heating the metals together. Alloys with Al, Sb, Pb, Hg, Na, and Zn have been described (Caron, *C. R.* 48, 440; 50, 547; Wöhler, *A.* 138, 253). Calcium is usually estimated either as carbonate or sulphate, or volumetrically, by $K_2Mn_2O_8Aq$, after ppn. as CaC_2O_4 and decomposition of this salt by H_2SO_4Aq.

Calcium, Alloys of, *v.* CALCIUM; *Combinations*, No. 4.

Calcium, Arsenates of. $CaHAsO_4$ and $Ca_3(AsO_4)_2$: *v.* ARSENATES, under ARSENIC, ACIDS OF.

Calcium, Arsenites of. $Ca_3(AsO_3)_2$; $Ca(AsO_2)_2$; and $Ca_2As_2O_5$: *v.* ARSENITES, under ARSENIC, ACIDS OF.

Calcium, Bromide of. $CaBr_2$. Mol. w. unknown, as compound has not been gasified. [676°–680°] (Carnelley, *C. J.* 29, 497; 33, 279). S.G. 3·32 (Kopp, *A.* 93, 129). S. (0°) 125; (20°) 141; (40°) 212; (60°) 277; (105°) 312 (Kremers, *P.* 103, 65). H.F. $[Ca,Br^2] = 140,850$; $[CaBr^2,Aq] = 165,360$ (Thomsen).

Formation.—$CaBr_2$ is formed by dissolving CaO or $CaCO_3$ in HBrAq, evaporating, and crystallising; or by decomposing Fe_2Br_4Aq by CaOAq.

Preparation.—1. 12½ parts Br and 1 part amorphous P are allowed to react in presence of H_2O; the solution is neutralised by $CaCO_3$ or CaO_2H_2, filtered from $Ca_3.2PO_4$, evaporated, and crystallised (Klein, *A.* 128, 237).—2. 20 parts S are dissolved in 240 parts Br, and the liquid is poured into thin milk of lime, containing 140 parts CaO; $CaSO_4$ is ppd. by alcohol, the solution is filtered off, evaporated, and crystallised (Faust, *Ar. Ph.* [2] 131, 216).

Properties.—White, lustrous, deliquescent, needles: very soluble in H_2O and alcohol. Absorbs NH_3 forming $CaBr_2.6NH_3$ (Rammelsberg, *P.* 55, 239). $CaBr_2Aq$ boiled with CaO_2H_2, and filtered, on cooling yields crystals of $CaBr_2.3CaO.15H_2O$.

Combinations. — With *water* to form $CaBr_2.6H_2O$. $[CaBr^2,6H^2O] = 25,600$; $[CaBr^2.6H^2O,Aq] = -1090$ (*Th.* 3, 251).

Calcium Bromide, hydrated, *v.* CALCIUM, BROMIDE OF, *Combinations.*

Calcium, Chloride of. $CaCl_2$. Mol. w. unknown, as compound has not been gasified. [719°–723°] (Carnelley, *C. J.* 29, 497). S.G. 2° 2·205 (Schiff, *A.* 108, 23). S.H. (23°–99°) ·1642 (Regnault, *A. Ch.* [3] 1, 129). S. (0°) 49·6; (10°) 60; (20°) 74; (30°) 93; (35°) 104; (40°) 110; (50°) 120; (60°) 129; (70°) 136; (80°) 142; (90°) 147; (95°) 151; (99°) 154 (Mulder, *J.* 1866. 66). H.F. $[Ca,Cl^2] = 169,820$; $[Ca,Cl^2,Aq] = 187,230$ (Thomsen).

Formation.—In making NH_3 by the action of CaO_2H_2 on NH_4ClAq; also as a by-product in many chemical manufactures.

Preparation.—1. Pure $CaCO_3$ is dissolved in pure HClAq; the solution is evaporated to dryness and heated to about 200°.—2. Ordinary marble or chalk is dissolved in HClAq, Cl is led into the acid liquid until all Fe and Mn salts are completely oxidised. Milk of lime is added to alkaline reaction, the whole is digested, the liquid is filtered from lime and ppd., oxides of Mg, Fe, and Mn, neutralised by HClAq, and evaporated as in 1.

Properties and Reactions.—A white, porous, very deliquescent, solid: after melting and cooling it is distinctly crystalline. Absorbs moisture rapidly: hence is much used for drying gases, &c.; if the $CaCl_2$ to be used must be free from CaO, *e.g.* for drying CO_2, it should be placed for some time in a stream of CO_2 and then of dry air at the ordinary temperature. $CaCl_2$ is very soluble in water and alcohol, much less soluble in HClAq. It is partly decomposed by heating in air (*v.* Weber, *B.* 15, 2316), more completely by heating in O, with production of CaO. Heated with $KClO_3$ or $KClO_4$, part of it is changed to CaO (Schulze, *J. pr.* [2] 21, 407). $CaCl_2Aq$ is used as a bath for maintaining temperatures above 100°; 50 parts $CaCl_2$ in 100 parts H_2O forms a solution boiling at 112°; 100 $CaCl_2$ in 100 water, B.P. 128°; 200 $CaCl_2$ in 100 H_2O, B.P. 158°; and 325 $CaCl_2$ in 100 H_2O, B.P. 180° (Magnus, *P.* 112, 408; Wüllner, *P.* 110, 564; Legrand, *A.* 17, 34).

Combinations.—1. With *water* to form hexagonal crystals of $CaCl_2.6H_2O$ $[CaCl^2, 6H^2O] = 21,750$ (*Th.* 3, 251); best prepared by evaporating a solution of $CaCO_3$, or CaO, in HClAq and crystallising. $CaCl_2.6H_2O$ melts at 28° (Tilden, *C. J.* 45, 268); heated to 200°, or placed *in vacuo*, the hydrate $CaCl_2.2H_2O$ remains. This hydrate is also produced, according to Ditte (*C. R.* 92, 242), by saturating HClAq with $CaCl_2$ at 12° and cooling. Hamerl (*Sitz. W.* (2nd part) 72, 667) says that $CaCl_2.4H_2O$ is formed by repeatedly melting and cooling $CaCl_2.6H_2O$. According to Dibbits (*Ar. N.* 13, 478) $CaCl_2.6H_2O$ loses $4H_2O$ in a current of dry air, and $6H_2O$ in dry air at 80°. S.G. $\frac{10°}{}$ of $CaCl_2.6H_2O$, 1·612 (Kopp, *A.* 93, 129). S.H. of $CaCl_2.6H_2O$ (−20° to 2°) ·345, (4°–28°) ·647; melted (34°–59°) ·5601, (34°–99°) ·552, (100°–127°) ·519 (Person, *C. R.* 23, 162). C.E. (cubical) for solid $CaCl_2.6H_2O$; $V_t = V_0 (1 + \cdot000\,645\,1t - \cdot000\,053\,77t^2 + \cdot000\,001\,906\,t^3)$ for interval 11°–26° (Kopp, *A.* 93, 129). H.F. $[Ca, Cl^2, 6H^2O] = 191,980$; $CaCl_2.6H_2O$ dissolves in water with disappearance of much heat $[CaCl^2.6H^2O,Aq] = -4,340$ (Thomsen). This salt mixed with snow produces great lowering of temperature; for use as a freezing mixture the salt is best prepared by boiling a conc. solution until temperature rises above 129°, then allowing to cool, shaking well as the solid forms. $CaCl_2.6H_2O$ is thus obtained as a fine dry powder; 4 parts are mixed with 3 parts dry snow. Hamerl (*Sitz. W.* (2nd part) 78, 59) observed −54·9° by mixing this salt with dry snow, both cooled under 0°, in the ratio $CaCl_2.6H_2O$: 8·45 H_2O (as snow). $CaCl_2.6H_2O$; S (0°) 72·8; (13·8°) 80·9; (24·5°) 89·5; (29·5°) 100 (Hamerl, *Sitz. W.* (2nd part) 72, 287).—2. With

ammonia forms $CaCl_2.8NH_3$; dissociated by heat into $CaCl_2$ and NH_3; NH_3 also removed by dissolving in H_2O and passing in a current of air (Weber, *B.* 15, 2316). Isambert (*C. R.* 66, 1259) describes $CaCl_2.4NH_3$ and $CaCl_2.2NH_3$; he gives these thermal values $\frac{1}{2}[CaCl^2, 2NH^3] = 14,000$; $\frac{1}{4}[CaCl^2, 4NH^3] = 12,200$; $\frac{1}{8}[CaCl^2, 8NH^3] = 11,000$ (*C. R.* 86, 968).—3. With *alcohol* to form $CaCl_2.2C_2H_6O$; decomposed by H_2O (Chodnew, *A.* 71, 241; Johnson, *J. pr.* 62, 264). Forms combinations also with *acetone* (Hlasiwetz, *A.* 76, 294).—4. With *lime* to form $CaCl_2.3CaO.15H_2O$; prepared by boiling $CaCl_2Aq$ with CaO_2H_2, filtering while hot, and allowing to cool; decomposed by H_2O or C_2H_6O (Beesley, *Ph.* 9, 568; Rose, *S.* 29, 155; Bolley, *D. P. J.* 153, 202; Grimshaw, *C. N.* 30, 280).—5. With *platinous chloride* to form $CaCl_2.PtCl_2.8H_2O$; M.P. = 100° (Nilson, *J. pr.* [2] 15, 260).

Calcium chloride, hydrated, *v.* CALCIUM, CHLORIDE OF; *Combinations*, No. 1.

Calcium, Cyanide of. $Ca(CN)_2$. Said to be obtained by heating Ca ferrocyanide and dissolving out with water (Schulz, *J. pr.* 68, 257). *v.* CYANIDES.

Calcium, Fluoride of. CaF_2. Mol. w. unknown, as compound has not been gasified. [abt. 902°] (Carnelley, *C. J.* 33, 280). S.G. $\frac{\text{abt. }15°}{4°}$ 3·15–3·18 (Schröder, *Dichtigkeitsmessungen* (Heidelberg, 1873); Kengott, *Sitz. W.* 10, 295). S.H. (21°–50°) ·209 (Kopp, *T.* 155, 71); (15°–99°) ·2154 (Regnault, *A. Ch.* [3] 1, 129). Index of refraction at 21° for line B = 1·432; line D = 1·4339; line F = 1·43709; line G = 1·43982; line H = 1·44204 (Stefan, *Sitz. W.* 63 (2nd part), 239). S. (15°) ·0004 (Wilson, *J.* 1850. 278). $[CaH^2O^2, 2HF] = 66,600$ (Guntz, *C. R.* 97, 1483, 1558; 98, 816).

Occurrence.—As *Fluorspar* in octahedra, cubes, and other forms of the monometric system, fairly widely distributed in many rocks; in small quantities in many mineral waters, plant-ash, bones (Lassaigne, *S.* 52, 141), enamel of teeth, &c.

Preparation.—1. As a gelatinous mass, by decomposing an aqueous solution of a Ca salt by that of a fluoride.—2. As a granular powder by digesting freshly ppd. $CaCO_3$ with HFAq.—3. In small octahedra by digesting the gelatinous pp. obtained in 1 with dilute HClAq for 10 hours at 240° (Sénarmont, *A. Ch.* [3] 32, 129; Scheerer a. Drechsel, *J. pr.* [2] 7, 63).

Properties and Reactions.—Transparent, colourless crystals, melting without decomposition at about 900°. Forms easily fusible mass with $BaSO_4$, $SrSO_4$, and many other insoluble compounds; hence much used as a flux. Soluble in aqueous solutions of NH_4 salts (Rose, *P.* 79, 112). Not decomposed by fusion with KOH or NaOH, but partially by fusion with excess of alkali carbonates. Decomposed, to CaO and HF, by heating to redness in steam; also decomposed by hot H_2SO_4Aq, but only very partially by boiling HClAq or HNO_3Aq. Said to be partly decomposed by $Al_2.3SO_4Aq$ (Friedel, *Bl.* [2] 21, 241).

Combinations.—With *hydrofluoric acid and water* to form $CaF_2.2HF.6H_2O$; produced in small crystals by evaporating a solution of CaO in large excess of HFAq; decomposed to CaF_2 and HFAq by hot water (Fremy, *A. Ch.* [3] 47 35).

Calcium, Hydrate of, CaO_2H_2, *v.* CALCIUM HYDROXIDE OF.

Calcium, Hydrosulphide of, *v.* CALCIUM SULPHYDRATE.

Calcium, Hydroxide of, CaO_2H_2. (*Slaked lime.*) Mol. w. unknown: compound is decomposed by heat. S.G. 2·078 (Filhol, *A. Ch.* [3] 21, 415). S.G. $\frac{\infty}{0}$ (crystalline) 2·236 (Lamy, *A. Ch.* [5] 14, 145). S. (15°) ·13; (54°) ·103; (100°) ·08 (Dalton, *New System*, 2, 331): S. (18°) ·13; (100°) ·07 (Bineau, *C. R.* 41, 509, *v.* also Lamy, *C. R.* 86, 333). H.F. $[Ca,O,H^2O] = 146,470$; $[CaO,H^2O] = 15,540$ (*Th.* 3, 251).

Preparation.—1. By adding to 1 part H_2O 3·1 parts CaO.—2. By allowing Ca to oxidise in moist air.—3. By adding KOHAq, or NaOHAq, to a conc. aqueous solution of a Ca salt, collecting pp., washing well, and drying at 100°. Gay-Lussac (*A. Ch.* 1, 334) obtained CaO_2H_2 in small six-sided plates by evaporating an aqueous solution over H_2SO_4 *in vacuo.*

Properties and Reactions.—A white, compact mass; slightly soluble in cold, less soluble in hot, water $[CaO^2H^2, Aq] = 2,290$ (*Th.* 3, 251). Strongly alkaline reaction. CaO_2H_2Aq neutralises acids with production of same quantity of heat as when 2NaOHAq, or 2KOHAq is used, viz. about 31,000 for H_2SO_4Aq, and about 27,900 for 2HClAq (Thomsen); also pps. many heavy metals as oxides or hydroxides, and saponifies fats. Moist CaH_2O_2 absorbs CO_2, forming $CaCO_3$ and H_2O. CaH_2O_2Aq forms insoluble salts when neutralised by H_2SiO_3Aq, H_3BO_3Aq, H_3PO_4Aq, &c.; pps. are also formed by adding animal char, sand, &c. CaH_2O_2 is soluble in solutions of cane sugar: on adding alcohol pps. are obtained, said to have the compositions

$CaO.C_{12}H_{22}O_{11}.H_2O$; $2CaO.C_{12}H_{22}O_{11}$;
$3CaO.C_{12}H_{22}O_{11}$; and $6CaO.C_{12}H_{22}O_{11}$

(Peleuze, *J.* 1864. 572; Bowin a. Loiseau, *A. Ch.* [4] 6, 203; Péligot, *A. Ch.* [3] 54, 383; Déon, *Bl.* [2] 17, 155; Berthelot, *A. Ch.* [3] 46, 173). CaH_2O_2 is much more soluble in glycerin than in water. At a bright red heat CaH_2O_2 is decomposed to $CaO + H_2O$. For reaction between Cl and CaH_2O_2 *v. Bleaching Powder* under HYPOCHLORITES, under CHLORINE, OXYACIDS OF.

Calcium, Iodide of. CaI_2. Mol. w. unknown, as compound has not been gasified. [631°] (Carnelley, *C. J.* 33, 279). S. (0°) 192; (20°) 204; (40°) 228; (43°) 286; (92°) 435 (Kremers, *P.* 103, 65). H. F. $[Ca, I^2] = 107,250$; $[Ca, I^2, Aq] = 134,940$ (*Th.* 3, 251).

Formation.—By the action of HIAq on CaO_2H_2; or of I on CaS suspended in water (Liès-Bodart a. Jobin, *A. Ch.* [3] 54, 363).

Preparation.—To 1 part amorphous P and 40 parts H_2O, 20 parts I are slowly added: the whole is digested at 100°; the colourless liquid is neutralised by milk of lime, and evapotraed in an atmosphere free from CO_2 (Liebig, *A.* 121, 222; Wagner, *C. C.* 1862. 143).

Properties and Reactions.—White, deliquescent mass; very soluble in water and alcohol; undecomposed when melted out of contact with air: melted in air gives CaO and I. Conc. CaI_2Aq dissolves I; on evaporation *in vacuo* crystals of a periodide are said to be obtained.

Absorbs $6NH_3$ (Isambert, *C. R.* 66, 1259). Forms an easily decomposed double compound with AgI; $CaI_2.2AgI.6H_2O$ (Simpson, *Pr.* 27, 120)

Calcium hydroxyhydrosulphide *v. post* under CALCIUM SULPHYDRATE.

Calcium, Oxides of. Two oxides are known; CaO a strongly basic compound, and CaO_2 which acts as a peroxide. CaO_2 cannot be formed by the action of O on CaO (*comp.* BaO_2).

I. CALCIUM MONOXIDE. CaO (*Lime, burnt lime*). Mol. w. unknown, as compound has not been gasified. S.G. 3·15 (Schröder, *P. Jubelbd.* 452); S.G. (crystalline, by heating $Ca2NO_3$) 3·251 (Brügelmann, *W.* 2, 466; 4, 277). S. variable according to state of aggregation of the CaO &c. Lamy (*A. Ch.* [5] 14, 145) gives the following numbers representing grams of CaO in 1000 grams of solution; CaO being made (1) by heating $Ca2NO_3$, (2) by heating $CaCO_3$, (3) by heating CaO_2H_2:—

Temp.	(1)	(2)	(3)
0°	1·362	1·381	1·430
10	1·311	1·342	1·384
15	1·277	1·299	1·348
30	1·142	1·162	1·195
45	0·996	1·005	1·033
60	0·844	0·868	0·885
100	0·562	0·576	0·584

H. F. [Ca, O] = 130,930; [Ca, O, Aq] = 149,260 (*Th.* 3, 251).

Preparation.—Pure marble, or Iceland spar, is strongly heated in a crucible with a hole in the bottom to allow escape of CO_2; or a piece of charcoal is placed in the crucible beneath the marble, CO is thus formed and sweeps out the CO_2 with it. $CaCO_3$ is not completely decomposed when heated in an atmosphere of CO_2; *v.* CALCIUM CARBONATE, under CARBONATES. Sestini (*Fr.* 4, 51) strongly heats powdered marble with sugar, washes with H_2O, dissolves in HNO_3Aq, pps. $CaCO_3$ by $(NH_4)_2CO_3Aq$, and strongly heats the dried pp. By strongly heating $Ca2NO_3$, in quantities of about 15–20 grams at a time, in a porcelain flask, Brügelmann (*W.* 2, 466; 4, 277) obtained cubical crystals of CaO; semitransparent, harder than the amorphous form, and less easily acted on by H_2O and CO_2.

Properties and Reactions.—White, amorphous (or crystalline *v. supra*), powder: does not fuse at full white heat. Strongly basic; reacts with most acids to form salts. CaO is decomposed by heating to whiteness with K; heated in Cl, $CaCl_2$ is formed. CaS is produced by heating with S, and CaS and $CaCO_3$ by heating in CS_2. CaO does not combine with O (*v.* Conroy, *C. J.* [2] 11, 809).

Combinations.—With *carbon dioxide* to form $CaCO_3$ (but dry CaO does not react with CO_2: Scheibler, *B.* 19, 1973); combination begins at about 400° (*v.* Birnbaum a. Mahn, *B.* 12, 1547); [CaO, CO^2] = 42,520 (*Th.* 3, 251). Heated with *silica* or silicates, silicates of Ca are formed, which in contact with water set to a hard compact mass (hydraulic mortars). With *water*, CaO_2H_2 is formed with production of much heat [CaO, H^2O] = 15,540 (Thomsen); the lime is said to be slaked.

II. CALCIUM DIOXIDE, CaO_2 (*Calcium peroxide*). Mol. w. unknown. Prepared by adding pure H_2O_2Aq to excess of CaOAq, or by adding excess of CaOAq to Na_2O_2Aq containing some HNO_3Aq; collecting pp., washing well with cold water, and heating the $CaO_2.8H_2O$ thus produced in a current of dry air free from CO_2 to 100°–120°. Forms a snow-white crystalline powder; does not melt at red heat, but gives off O and forms CaO. The hydrate $CaO_2.8H_2O$ is slightly soluble in H_2O, in contact with H_2O it slowly decomposes to CaO_2H_2Aq and H; soluble in NH_4ClAq, but not in NH_3Aq; dissolves easily in dilute acids, even in $H.C_2H_3O_2Aq$, without evolution of O. It forms prismatic dimetric crystals, isomorphous with $BaO_2.8H_2O$ and $SrO_2.8H_2O$ (Schöne) (Thénard, *A. Ch.* [2] 8, 306; Conroy, *C. J.* [2] 11, 808; Schöne, *B.* 6, 1172).

Calcium oxide, hydrated, CaO_2H_2, *v.* CALCIUM, HYDROXIDE OF.

Calcium, Oxybromide of, $CaBr_2.3CaO.15H_2O$ *v.* CALCIUM, BROMIDE OF; *Properties.*

Calcium, Oxychloride of, $CaCl_2.3CaO.15H_2O$, *v.* CALCIUM, CHLORIDE OF; *Combinations*, No. 4.

Calcium, Oxysulphides of, *v.* CALCIUM POLYSULPHIDES; under CALCIUM, SULPHIDES OF.

Calcium, Phosphide of. When Ca and P are heated under rock oil, and the unacted-on P is dissolved out by CS_2, a black powder remains which is acted on by H_2O and acids with production of PH_3; this black powder is said by Vigier to be Ca phosphide (*Bl.* 1861. 5). By strongly heating CaO in P vapour, a brown, amorphous mass is obtained; when heated with conc. HClAq, non-inflammable PH_3 is evolved, but with dilute HClAq the gas evolved takes fire. Probably in the first case liquid PH_2 is formed and at once decomposed to gaseous PH_3 and solid P_2H; in the second case the decomposition of PH_2 proceeds more slowly, so that some is carried into the air with the PH_3 and causes the combustion (Thénard, *A. Ch.* [3] 14, 12). The brown substance got by heating CaO in P vapour is said to be a mixture of CaP and $Ca_2P_2O_7$ (Thénard, *l.c.*): this brown substance is described by Thénard as a very hard solid; unchanged in dry air; deliquescent in moist air; burns when heated in air; acted on by water free from air gives CaOAq and PH_2, PH_2 decomposes to PH_3 and P_2H, and the P_2H is decomposed by the CaOAq to $Ca(H_2PO_2)_2Aq$ and H.

Calcium, Salts of. Compounds obtained by replacing H of acids by Ca. These salts form one series CaX_2 where $X_2 = Cl_2$, $(NO_3)_2$, SO_4, CO_3, $\frac{2}{3}PO_4$, &c. They are generally formed by the action of CaO or CaO_2H_2 on the acids in aqueous solution, or by the decomposition of salts of the heavier metals by CaO_2H_2Aq. As none of the Ca salts has been gasified, the formulæ are based partly on similarities between these salts and those of analogous metals which form gasifiable compounds, chiefly Zn, Cd, and Hg, and partly on the fact that the general formula CaX_2 is the simplest that can be given, provided the atomic weight of Ca is about 40 (this has been established by analyses of $CaCl_2$, $CaCO_3$ &c. and by determinations of the S.H. of the metal; *v.* CALCIUM). Salts of Ca derived from a great many acids are known; they are well marked stable bodies; many form double salts; few basic salts are known. Most of the Ca salts are soluble in water; the more insoluble are the arsenite, carbonate, fluoride, oxalate, phosphate, sulphate, and sulphite. With the exception of CaF_2 all the salts are more or less

soluble in dilute acids. The Ca salts of non-volatile acids are generally undecomposed by heat. Ca salts derived from a great many acids are known (v. BORATES, CARBONATES, PHOSPHATES, SULPHATES, &c., &c.).

Calcium, Selenide of. CaSe. Mol. w. unknown. White solid, rapidly changing in air, prepared by heating $CaSeO_4$ to dull redness in H; [Ca,Se] = 78,000 (Fabre, *C. R.* 102, 1469).

Calcium, Seleniocyanide of. (? $CaSe_2(CN)_2$). Probably exists. Data very meagre (Crookes, *J. pr.* 53, 161).

Calcium, Sulphides of. One calcium sulphide, CaS, is known as a solid; solutions which most probably contain CaS_4 and CaS_5, respectively, have been prepared. The sulphides of Ca are decidedly less basic than those of Ba, *e.g.* they do not react with the sulphides of the negative metals As and Sb to form thio-salts.

I. CALCIUM MONOSULPHIDE. CaS. Mol. w. unknown. H.F. solid, from solid materials: [Ca,S] = 92,000 (Sabatier, *A. Ch.* [5] 22, 598).

Preparation.—1. H_2S is passed over CaO_2H_2 kept at about 60°; the sole products are CaS and H_2O. If the reacting bodies are *perfectly* dry the change does not occur (Veley, *C. J.* 47, 478).—2. By gently heating crystals of $CaS_2H_2.6H_2O$ (*q.v.*) in H_2S; the product contains some CaO_2H_2 (Divers a. Shimidzu, *C. J.* 45, 270). Schöne's method, heating $CaCO_3$ in a mixture of CO_2 and H_2S (*P.* 112, 193) is said by Divers to yield a mixture of CaS and CaO in the ratio 11CaS:5CaO (*C. J.* 45, 282).

Properties and Reactions.—A white amorphous solid; soluble in water with gradual decomposition, giving H_2S, and solution of Ca.SH.OH (*q.v.*) which then slowly decomposes in air forming CaS_2O_3Aq and CaS_5Aq (Divers a. Shimidzu, *l.c.*). The impure CaS produced by heating CaO with CS_2, or $CaSO_4$ with C, is not soluble in, although it is partially decomposed by, water. Perfectly dry CaS does not absorb CS_2; but in presence of H_2O a basic calcium thiocarbonate, $2CaO_2H_2.CaCS_3.10H_2O$, is produced (Veley, *C. J.* 47, 486). Sabatier (*A. Ch.* [5] 22, 598) gives the thermal value [Ca,S] = 92,000; [CaS, Aq] = 6,010 (? pure materials).

II. CALCIUM POLYSULPHIDES. When CaS (prepared by heating CaO in CS_2 and CO_2 and therefore containing some CaO) is boiled with S and H_2O, it dissolves, forming an orange-red liquid; the quantity of S which goes into solution corresponds with that required to form CaS_4 and CaS_5; if more S is used it is deposited on cooling the liquid; if less S than S_3 to CaS is used, some of the CaS remains undissolved. Both solutions are decomposed on concentration with ppn. of CaO_2H_2 and S, and evolution of H_2S (*v.* Schöne, *P.* 117, 58). Warm CaS_2H_2Aq dissolves S very readily, forming a solution of CaS_5 and evolving H_2S; this solution is completely decomposed (if cold and dilute) by H_2S forming CaS_2H_2Aq with ppn. of S (Divers a. Shimidzu, *C. J.* 45, 270).

CaS_5Aq is decomposed in contact with air. By boiling 3 parts CaO, 1 part S, and 20 parts H_2O for some time, and allowing to stand for several days, orange-red needles are obtained of $3CaO.CaS_4.12H_2O$ (Herschel, *N. Ed. P. J.* 1, 8; Schöne, *P.* 117, 58), $2CaO.CaS_3$. 10 or 11 H_2O according to Geuther (*A.* 224, 178). If CaS (prepared by action of CS_2 and CO_2 on CaO) is boiled with much water and filtered hot, $CaSO_4$ is said to separate out and then yellow needles of $5CaO.CaS_5.20H_2O$ (H. Rose, *P.* 55, 433), or $4CaO.CaS_4.18H_2O$ (Schöne, *P.* 117, 58), or $3CaO.CaS_3$, 14 or 15 H_2O (Geuther, *A.* 224, 178). These oxysulphides are easily decomposed.

Calcium, Sulphocyanide of. $Ca(CNS)_2$. By saturating HCNSAq with $CaCO_3$, *v.* SULPHOCYANIDES, under CYANIDES.

Calcium Sulphydrate (or *hydrosulphide*); and **Calcium hydroxy-sulphydrate** (or *hydroxy-hydrosulphide*). $CaS_2H_2.6H_2O$, and $Ca.SH.OH.3H_2O$. By passing H_2S into a solution of CaO containing solid CaH_2O_2, $CaS_2H_2.6H_2O$ is formed: 1 part CaO is added to 3-4 parts warm water; when cold, H_2S is passed into the semi-solid substance until all has dissolved; more CaO is added, little by little, the whole being surrounded by ice, and H_2S is passed in until a little CaO remains undissolved; the liquid is quickly decanted into a tube kept in ice; the crystals which separate are drained and a current of dry H_2S is swept over them at 0°. Air must be excluded during the entire operation (Divers a. Shimidzu, *C. J.* 45, 270; Veley, *C. J.* 47, 478). $CaS_2H_2.6H_2O$ forms colourless prismatic crystals, which melt in their water of crystallisation, giving off H_2S and forming $Ca.SH.OHAq$ and CaO_2H_2. At about 15°-18°, H_2S is evolved even in an atmosphere of H_2S. $CaS_2H_2.6H_2O$ is very soluble in water and alcohol. CaS_2H_2Aq is slowly oxidised in contact with air, giving a little CaS_2O_3Aq and CaS_xAq. Thomsen (*Th.* 3, 251) gives the thermal value $[Ca,S^2,H^2,Aq] = 115,250$.

References.—Pelouze, *C. R.* 62, 108; H. Rose, *P.* 55, 133; Berzelius, *S.* 34, 12; *P.* 6, 442; Böttger, *A.* 29, 79; 33, 344.

When a stream of H is passed through an ice-cold solution of CaS_2H_2, crystals of $Ca.SH.OH.3H_2O$ are formed, and H_2S is evolved. The same compound is formed by the combination of H_2O with CaS, as in the interior of heaps of soda-waste; and by the mutual action of CaO_2H_2 and H_2S, as in the purification of coal gas. Calcium hydroxysulphydrate crystallises in colourless four-sided prisms; it is soluble in water with decomposition into CaS_2H_2Aq and CaO_2H_2; insoluble in, but slowly decomposed by, alcohol (CaS_2H_2 goes into solution and CaO_2H_2 remains; Divers a. Shimidzu, *C. J.* 45, 270). It absorbs CS_2 forming a basic thiocarbonate $2CaO_2H_2.CaCS_3.10H_2O$; it is the active agent for absorbing CS_2 in gas-purification (Veley, *C. J.* 47, 478). M. M. P. M.

CALLUTANNIC ACID $C_{14}H_{14}O_9$. Occurs in *Calluna vulgaris*, the common Ling. The green parts are extracted with alcohol, water is added, and from the filtrate the lead salt is ppd. by $Pb(OAc)_2$. Amber-coloured mass. Its solution in alkalis rapidly absorbs oxygen from the air. Reduces $AgNO_3Aq$. Fe_2Cl_6 gives a green colour. Dyes mordanted wool sulphur-yellow.—

Salts.— $(PbC_{14}H_{12}O_9)_2(PbO)_3aq(?)$—
$(PbC_{14}H_{12}O_9)_3(PbO)_5 2aq(?)$—
$Sn(C_{14}H_{12}O_9)_2(SnO_2)_6 2aq(?)$.

Boiling dilute mineral acids convert callutannic acid into calluxanthin $C_{14}H_{10}O_7$, a yellow floccu-

lent pp., sl. sol. cold water, v. sol. hot water and alcohol. Its alkaline solutions rapidly absorb oxygen from the air (Rochleder, *A.* 84, 354).

CALMUS *v.* CALAMUS.

CALOMEL. Mercurous chloride (HgCl). *V.* MERCURY, CHLORIDES OF.

CALOPHYLLUM RESIN $C_{14}H_{18}O_4$. [105°]. S.G. 1·12. A resin from *Calophyllum calaba* or *longifolium* of South America. Said to give butyric acid on oxidation (Levy, *C. R.* 18, 242).

CALORIMETER. Instrument for measuring quantities of heat. *V.* PHYSICAL METHODS, *Sect.* THERMAL.

CALYCIN $C_{18}H_{12}O_5$ [240° uncor.]. Occurs in a yellow lichen, *Calycium chrysocephalum*, from which it is extracted by boiling ligroïn (Hesse, *B.* 13, 1816). Sublimable. Yellow needles or prisms. S. sol. cold petroleum spirit, petroleum ether, ether, alcohol, and acetic acid, more easily in the hot solvents. By strong aqueous KOH it is split up into oxalic and phenyl-acetic acids. Carbonated alkalis give salts of calycic acid.

CAMELLIN $C_{53}H_{84}O_{19}$. A glucoside occurring in the seeds of *Camellia japonica* (Katzujama, *Ar. Ph.* [3] 13, 334). Extracted by alcohol, and ppd. by lead acetate. White powder with bitter taste, insol. water. Somewhat resembles digitalin.

CAMPHANIC ACID $C_{10}H_{14}O_4$ *i.e.*

$C_8H_{13}(CO_2H)<\begin{matrix}O\\ |\\ CO\end{matrix}$. *Oxy-camphoric anhydride.*

From bromo-camphoric anhydride, the product of the action of bromine on camphoric anhydride, by treatment with water (Wreden, *A.* 163, 330; Woringer, *A.* 227, 3). From campholic acid and bromine (Kachler, *A.* 162, 264). Formed also as a by-product in the preparation of camphoric acid by oxidation of camphor with HNO_3 (Roser, *B.* 18, 3112). According to Fittig (*A.* 172, 151) it is a lactonic acid, formed *viâ* $C_8H_{13}Br<\begin{matrix}CO\\ CO\end{matrix}>O$ and $C_8H_{13}(OH)(CO_2H)_2$.

Properties.—Feathery crystals or prisms (from water). Monoclinic, $a:b:c = 1·2723:1:1·522$. $\beta = 66°34'$.

Salt.—$BaA'_2\,3\frac{1}{2}aq$

Reaction.—1. On distillation camphanic acid gives CO_2, campholactone $C_8H_{14}<\begin{matrix}O\\ |\\ CO\end{matrix}$, and lauronolic acid $C_8H_{13}CO_2H$.—2. $K_2Cr_2O_7$ and H_2SO_4 oxidise it to camphoronic acid $C_9H_{14}O_6$ (Bredt, *B.* 18, 2989).

CAMPHENE *v.* TERPENES.

CAMPHENOL *v.* BORNEOL and CINEOL.

CAMPHENYL-*p*-TOLYL-AMIDINE

$C_9H_{15}C(NH_2):NC_7H_7$ [115°]. Fine white glistening needles (from ligroïn). Formed by heating campholenonitrile $C_9H_{15}CN$ with *p*-toluidine hydrochloride at 250° (Goldschmidt a. Koreff, *B.* 18, 1633).

CAMPHIC ACID $C_{10}H_{16}O_2$. S. ·14 at 19°. $[\alpha]_D = 15°45'$ (in alcoholic solution). Formed together with camphoric acid by passing air through a boiling solution of sodium camphor, $C_{10}H_{15}NaO$ in xylene. Thick mass, v. sol. alcohol and ether. $KMnO_4$ oxidises it to camphoric acid. The calcium salt distilled with calcium formate gives camphor and camphrene $C_9H_{14}O$ (c. 233°) (Montgolfier, *A. Ch.* [5] 14, 70; *C. R.* 88, 915).

CAMPHILENE *v.* TERPENES.

CAMPHIMIDE $C_{10}H_{15}N$ or $C_8H_{14}<\begin{matrix}C\\ \|\\ C\end{matrix}>NH$ (?)

Formed together with dicamphorilimide by distilling the hydrochloride of amido-camphor (*v.* CAMPHOR) with steam (Schiff, *B.* 13, 1405).

CAMPHINE *v.* TERPENES.

CAMPHO-CARBOXYLIC ACID *v.* CAMPHOR CARBOXYLIC ACID.

(α)-**CAMPHOGLYCURONIC ACID** $C_{16}H_{24}O_8$. [130°]. S. 5. $[\alpha]_D = -33°$. Occurs, together with uramido-camphoglycuronic acid in the urine of dogs that have taken camphor (Schmiedeberg a. Meyer, *H.* 3, 422). Small thin laminæ (containing aq); v. e. sol. alcohol and hot water, insol. ether. Boiling dilute HCl splits it up into glycuronic acid $C_6H_{10}O_7$ and crystalline campherol $C_{10}H_{16}O_2$ [198°]. HNO_3 oxidises it to camphoric acid.—BaA″.—BaA″ 2aq.—AgHA″ $x$aq.

(β)-Camphoglycuronic acid $C_{16}H_{24}O_8$. An amorphous modification of the preceding, formed by warming it with baryta.—AgHA″ 3aq: crystals, more soluble than the Ag salt of the (α) acid.

CAMPHOL a name for BORNEOL (*q.v.*).

CAMPHOLACTONE $C_8H_{14}<\begin{matrix}CO\\ |\\ O\end{matrix}$. [50°]. (230°-235°). From camphanic acid by distillation, together with lauronolic acid (Woringer, *A.* 227, 10). Slender needles (from water). Has a pungent odour of camphor. Like other lactones, its solution becomes cloudy when gently heated, but the oily drops afterwards dissolve up again. Volatile with steam. K_2CO_3 separates it from its aqueous solution. When boiled with baryta the salt of the corresponding oxy-acid, $C_8H_{14}(OH)CO_2H$, is formed.

CAMPHOLENE C_9H_{16} (136°). V.D. 4·35. Prepared by the action of dehydrating agents on campholic acid (Delalande, *A.* 38, 340) and by distilling potassium campholate with soda-lime (Kachler, *A.* 162, 266). Probably identical with the hydrocarbon got by distilling the calcium salt of campholenic acid (Goldschmidt, *B.* 20, 483). The name campholene has also been given to C_8H_{14} (c. 123°) obtained by the action of dehydrating agents on camphoric acid and its amides (Ballo, *B.* 12, 324).

CAMPHOLENIC ACID $C_{10}H_{16}O_2$ *i.e.* $C_9H_{15}.CO_2H$ or $C_8H_{13}(CO_2H):CH_2$. *Oxy-camphor.* (c. 250°). Colourless oil. Formed by saponification of its nitrile which is obtained by heating camphoroxim with acetyl chloride. Formed also by treating an alcoholic solution of (β)-di-bromo-camphor with sodium-amalgam (Goldschmidt a. Zürrer, *B.* 17, 2069; Kachler a. Spitzer, *B.* 17, 2400; *M.* 3, 216; 4, 643). The Ca salt on dry distillation yields C_9H_{16}, possibly campholene (Goldschmidt, *B.* 20, 483). Oxidising agents give oxy-camphoronic acid. At 250° the NH_4 salt gives the amide [127°].—NH_4A'.—BaA'_2 4aq.

Amide $C_9H_{15}.CONH_2$. *Isocamphoroxim* [125°]. Glistening plates; sol. alcohol, ether, and conc. acids. Formed by heating the nitrile with alcoholic KOH, or by heating the ammo-

nium salt of the acid to 250°. By distillation with P_2S_5 it yields the nitrile (Nägeli, *B.* 17, 805; Goldschmidt a. Zürrer, *B.* 17, 2069).

Nitrile.—$C_9H_{15}.CN$. (216°). *Formation.*—1. By heating camphoroxim with AcCl which removes H_2O.—2. By distilling campholenamide (isocamphoroxim) with P_2S_5. *Reactions.*—1. By heating with alcoholic KOH it is converted into campholenamide. By long boiling with alcoholic KOH it yields campholenic acid.—2. By heating with *hydroxylamine* it gives an amidoxim $C_{10}H_{18}N_2O$ which crystallises in white plates melting at [101°].—3. Reduced in alcoholic solution by Zn and HCl to the amine $C_9H_{15}.CH_2.NH_2$ (Goldschmidt a. Zürrer, *B.* 17, 2069; Goldschmidt a. Koreff, *B.* 18, 1634).—4. Successive treatment with *sodium amalgam* and HCl yields $C_{16}H_{27}N_3Cl_2$, the hydrochloride of camphyl-di-phenyl-hydrazinamine $C_9H_{14}(CH_2NH_2)N_2H_2Ph$. [157°] (Balbiano, *G.* 17, 155).

Nitro-campholenic acid $C_{10}H_{15}(NO_2)O_2$. *Nitro-oxy-camphor.* [164°] (Z.); [170°] (K. a. S.). Formed by nitration of campholenic acid (Zürrer, *B.* 18, 2228; Kachler a. Spitzer, *M.* 4, 643; *B.* 15, 2336; Swarts, *B.* 15, 2135). Monoclinic pyramids, $a:b:c = \cdot76:1:\cdot43$; $\beta = 89° 18'$. Sol. hot alcohol and ether. Reduced by tin and HCl to amido-campholenic acid whose hydrochloride crystallises in laminæ [250°].

CAMPHOLIC ACID $C_{10}H_{18}O_2$. Mol. w. 170. [95°] (K.); [106°] (M.). $[\alpha]_j = 50°$ (in alcohol).

Formation.—1. By passing camphor-vapour over nearly red-hot potash-lime (Delalande, *A. Ch.* [3] 1, 120).—2. By adding potassium in small pieces to a solution of camphor (1 pt.) in boiling petroleum (3 pts.) at 130° (Malin, *A.* 145, 201).—3. By boiling camphor with alcoholic KOH (Kachler, *A.* 162, 259). — 4. By heating camphor with Na at 280° (Montgolfier, *A. Ch.* [5] 14, 99).

Properties.—Monoclinic prisms (from dilute alcohol) or nodular groups of laminæ (from ether-alcohol). V. sl. sol. water; volatile with steam.

Reactions.—1. HNO_3 gives first camphoric and then camphoronic acids. — 2. Moist Br gives at first camphoric acid, then bromo-camphoric anhydride, and lastly oxy-camphoric anhydride $C_{10}H_{14}O_4$.—3. P_2O_5 gives campholene; red-hot *soda-lime* acts similarly.

Salts. — $KA'2aq$: laminæ. — CaA'_2aq.— AgA'.

Chloride (224°) (Kachler, *A.* 162, 265).

CAMPHOR $C_{10}H_{16}O$. Mol. w. 152. [175°]. (204°). S.G. $\frac{10}{}$ ·992. S. ·1. S. (alcohol of S.G. ·806) 120. V.D. 5·32. R_∞ 78·11 (in a 32·3 p.c. benzene solution) (Kanonnikoff). $[\alpha]_D = 55{\cdot}4 - {\cdot}1372\,q$ (where q = no. of grms. of alcohol in 100 grms. of solution).

Occurs in the wood and bark of *Laurus camphora*, from which it is extracted by distillation with steam followed by sublimation. Varieties of camphor occur also in several essential oils (*v. infra*). Camphor may be recovered from its bromo-derivative by the action of nascent H or of alcoholic KOH (Schiff, *B.* 13, 1407; 14, 1377). Camphor is also formed by distilling calcium camphate with calcium formate and by oxidising dextro- and lævo-rotatory borneols (Montgolfier, *C. R.* 88, 915; *A. Ch.* [5] 14, 20).

Properties.—Hexagonal prisms, terminated by hexagonal pyramids (Descloizeaux, *A. Ch.* [3] 56, 219; Cazeneuve a. Morel, *C. R.* 101, 438). Tough, with peculiar odour; sublimes at ordinary temperatures. Small pieces rotate upon pure water. V. sl. sol. water, v. sol. ordinary solvents. Camphor is dextro-rotatory, the rotation varying greatly with the nature and strength of the solvent (Arndtsen, *A. Ch.* [3] 54, 403; Landolt, *A.* 189, 334). Its refractive power is that of a saturated compound (Gladstone, *C. J.* 49, 621).

Reactions.—1. Camphor (5 kilos.) gives, when oxidised by HNO_3, (1·7 kilos. of) pure camphoric acid insol. cold water, and (1·8 kilos. of) crude camphoronic acid. Besides camphoronic acid the soluble portion contains (·1 kilo. of) dinitroheptoic acid, and (·2 kilo. of) acids $C_9H_{14}O_6$ (hydro-oxycamphoronic acid), $C_9H_{12}O_7$, $C_7H_{12}O_5$ (?) [145°], and another acid. A very small quantity (2 g.) of mesocamphoric acid, $C_{10}H_{16}O_4$, is also got. This forms woolly needles, soluble in cold water [120°].—2. By oxidation with CrO_3 it gives camphoronic acid $C_9H_{12}O_5$ and hydro-oxy-camphoronic $C_9H_{14}O_6$ but not adipic acid (Kachler, *B.* 13, 487; *cf.* Ballo, *B.* 12, 1597). Alkaline $KMnO_4$ gives camphoric acid (Grosser, *B.* 14, 2507).—3. The chief products of the dry distillation of camphor with $ZnCl_2$ (2 pts.) are *m*-methyl-isopropyl-benzene (*m*-cymene) and (1:2:4)-di-methyl-ethyl-benzene (laurene), together with smaller quantities of (1:2:3:5)-tetra-methyl-benzene (isodurene), carvacrol, camphorone, and various other bodies (Armstrong a. Miller, *B.* 16, 2255) such as CH_4, benzene, toluene, xylene, and ψ-cumene (Fittig, *A.* 145, 129; Rommier, *Bl.* 12, 383; Lippmann a. Longuinine, *Z.* [2] 5, 413; Montgolfier, *A. Ch.* [5] 14, 87).—4. By the action of *iodine* it yields a hydrocarbon $C_{10}H_{16}$, carvacrol, (1:2:4)-di-methyl-ethyl-benzene, (1:2:3:5)-tetra-methyl-benzene, and traces of ordinary cymene (A. a. M.; *cf.* Armstrong a. Kaskell, *B.* 11, 151; Rayman a. Preis, *B.* 13, 346).—5. By treatment with P_2O_5 ordinary cymene is formed, which is also the chief product of the action of P_2S_5 but accompanied in the latter case by small quantities of *m*-methyl-isopropyl-benzene and tetra-methyl-benzene (Delalande, *A. Ch.* [3] 1, 368; Armstrong a. Miller, *B.* 16, 2255).—6. By distillation over *red-hot zinc-dust* a mixture is formed of toluene, *p*-xylene, cymene, and a little benzene (Schrötter, *B.* 13, 1621).—7. Conc. H_2SO_4 forms camphrene or camphorphorone $C_9H_{14}O$ (Chautard, *C. R.* 44, 66; Schwanert, *A.* 123, 298).—8. Boiling alcoholic KOH forms campholic acid and borneol (Berthelot, *A. Ch.* [3] 56, 94; *J. L.* [2] 17, 390; Montgolfier, *Bl.* [2] 18, 114; 25, 12; Wheeler, *A.* 146, 84; Kachler, *A.* 162, 268). Campholic acid is also formed by passing camphor-vapour over heated soda lime. 9. Cl has no action, but in presence of alcohol or PCl_3 chlorination ensues (Claus, *J. pr.* 25, 257).—10. HClO forms chloro-camphor.—11. Br forms $C_{10}H_{16}OBr_2$ which readily splits up into HBr and bromo-camphor.—12. ICl at 250° forms CCl_4, C_2Cl_6, and C_6Cl_6.—13. PCl_5 forms $C_{10}H_{16}Cl_2$.—14. Camphor absorbs HCl (Bineau, *A. Ch.* [3] 24, 328). Aqueous HCl at 170°

splits it up into H_2O and cymene (Alexejeff, *J. R.* 12, 187).—15. Camphor absorbs SO_2, becoming liquid.—16. It also absorbs NO_2.—17. Conc. HIAq at 200° forms $C_{10}H_{18}$ (163°), C_9H_{16} (135°–140°), and $C_{10}H_{20}$ (170°–175°) (Weyl, *Z.* [2] 4, 496; *B.* 1, 96).—18. *Sodium-amalgam* has no action.—19. Na acting at 90° on a solution of camphor in toluene forms sodium-camphor and sodium borneol (Baubigny, *Z.* [2] 2, 408; 4, 298) (*cf.* p. 672).—20. CO_2 gas passed into the product of the action of Na on camphor in toluene forms the carboxylic acids of camphor and of borneol (Baubigny, *Z.* [2] 4, 482, 647). Air passed into the same mixture forms camphoric acid (Montgolfier, *A. Ch.* [5] 14, 75).—21. Camphor does not combine with $NaHSO_3$ (Fittig a. Tollens, *A.* 129, 371).—22. AcCl has no action.—23. Converted in the animal economy (of a dog) into camphoglycuronic acid (*q. v.*).—24. Melted camphor absorbs BF_3 forming $C_{10}H_{16}OBF_3$ [70°]; when this is heated for 24 hours there is formed cymene and its polymerides, C_6H_{10}, C_7H_{12}, and other hydrocarbons (Landolph, *C. R.* 86, 539).—25. *Chloral hydrate* forms an unstable molecular compound with camphor. It is a viscous liquid, sol. alcohol and $CHCl_3$, insol. water (Cazeneuve a. Imbert, *Bl.* [2] 34, 209; Zeidler, *J.* 1878, 645).—26. By heating with *ammonium formate* at 220°–240° it yields formyl-bornylamine

$$C_8H_{14}\left\langle\begin{array}{l}CH_2\\ |\\ CH.NHCHO\end{array}\right.$$

(Leuchart a. Bach, *B.* 20, 104).—27. It does not react with phenyl-cyanate (L. a. B.).—28. Hydroxylamine forms an oxim, *v.* CAMPHOROXIM.

Phenyl-hydrazide $C_{10}H_{16}:N_2HPh$. (233°) at 10 mm. From camphor and phenyl-hydrazine. Oil. Split up by dilute HCl into camphor and phenyl-hydrazine, and by dry HCl into aniline and the nitrile of campholenic acid (Balbiano, *G.* 16, 132).

Constitution.—The action of hydroxylamine on camphor coupled with the fact that camphor does not combine with $NaHSO_3$ indicates that it is a ketone. The ready formation of benzene derivatives indicates a six-carbon ring. Its optical properties are those of a saturated compound, *v.* also TERPENES.

The two following formulæ amongst others have been proposed for camphor:

$$\begin{array}{l}CH_2.C(C_3H_7).CH_2\\ |\qquad\quad |\qquad\quad |\\ CH_2.C(CH_3).CO\end{array}$$

(Schiff, *A.* 226, 249; Kanonnikoff, *J. pr.* [2] 32, 511; *cf.* Kekulé, *B.* 6, 931);

$$\begin{array}{l}CH_2.CH_2.CH.CH_2\\ \qquad |\qquad\quad |\quad\ \ |\\ CH_3.CH.CH_2.CMe.CO\end{array}$$

(Armstrong a. Miller, *B.* 16, 2255). *V.* also TERPENES.

Chloro-camphor $C_{10}H_{15}ClO$. [95°]. From camphor and conc. HClOAq (Wheeler, *Am. S.* [2] 45, 48; *A.* 146, 81). Crystalline powder (from alcohol); at 200° it gives off HCl. Decomposed by alcoholic $AgNO_3$.

(α)-Chloro-camphor $C_{10}H_{15}ClO$. [84°]. (C.); [93°] (B.). (246°). $[\alpha]_j = 90°$. Formed by passing dry Cl into a solution of camphor (760g.) in absolute alcohol (230g.) (Cazeneuve, *C. R.* 94, 1530; *Bl.* [2] 38, 9; 44, 161). Formed also by heating chloro-camphor carboxylic acid (Schiff a. Puliti, *B.* 16, 887; Balbiano, *G.* 17, 95). Hard, brittle, monoclinic needles; smelling like camphor; volatile with steam. Not decomposed by alcoholic $AgNO_3$. Sodium-amalgam reduces it to camphor; the copper-zinc couple, and hot soda-lime, act similarly. Alcoholic KOH at 180° gives borneol. Phenyl-hydrazine forms $C_{10}H_{15}(N_2HPh)(N_2H_2Ph)$ [56°] (B.).

(β)-Chloro-camphor $C_{10}H_{15}ClO$. [100°]. (246°). $[\alpha]_j = 57°$. Deposited from the mother-liquor after the preceding has separated (Cazeneuve, *C. R.* 95, 1358; *Bl.* [2] 39, 116). Soft, minute, needles, more soluble than the preceding; miscible with boiling alcohol. Not decomposed by alcoholic $AgNO_3$, but converted by boiling alcoholic KOH into the preceding body. Phenyl-hydrazine produces the same compound [56°] as with the preceding (B.).

(α)-Di-chloro-camphor $C_{10}H_{14}Cl_2O$. [96°]. S.G. 4·2. $[\alpha]_j = 57·3°$ (in alcohol or chloroform). Formed by passing dry chlorine for several hours into camphor dissolved in absolute alcohol at 80°–90°. The product is ppd. by water and crystallised from alcohol (Cazeneuve, *C. R.* 94, 730, 1058; *Bl.* [2] 37, 454). Trimetric prisms (from alcohol); $a:b:c = 1·6358:1:1·4820$; sl. sol. cold, v. sol. hot, alcohol; almost insol. water but rotates upon it. Above 150° it blackens, giving off HCl. Insol. HOAc (difference from camphor). It forms a liquid combination with aldehyde.

(β)-Di-chloro-camphor $C_{10}H_{14}Cl_2O$. [77°]. $[\alpha]_j = 57·4°$ (in alcohol); 60·6° (in $CHCl_3$). Ppd. by adding water to the mother-liquor from which the preceding has crystallised (Cazeneuve, *C. R.* 94, 1360; *Bl.* [2] 38, 8). Crystallises from alcohol with difficulty; v. e. sol. alcohol, ether, and chloroform; liquefied by chloral-hydrate (difference from the preceding).

Tri-chloro-camphor $C_{10}H_{13}Cl_3O$. [54°]. $[\alpha]_j = 64°$ (in alcohol). Formed by saturating chloro-camphor with chlorine at 100° (Cazeneuve, *C. R.* 99, 609). Minute crystals, insol. water, sol. other menstrua. Gives off HCl when heated.

Bromo-camphor $C_{10}H_{15}BrO$. [76°]. (274°). S.G. 1·44 R_∞ 88·5 (in a 7·37 p.c. alcoholic solution) (Kanonnikoff, *J. pr.* [2] 32, 504). $[\alpha]_D = 139°$. Formed by heating camphor dibromide at 100° (Perkin, *C. J.* 18, 92; Maisch, *C. C.* 1873, 437). Monoclinic prisms (from alcohol); m. sol. alcohol, v. sol. $CHCl_3$ and benzene; may be sublimed (Montgolfier, *Bl.* [2] 23, 253).

Reactions.—1. *Sodium-amalgam* reduces it, in alcoholic solution, to camphor; alcoholic KOH also gives camphor. Sodium added to its solution in toluene gives sodium camphor (R. Schiff, *B.* 13, 1407).—2. PCl_5 has no action even at 100° (Schiff, *B.* 14, 1378; Kachler a. Spitzer, *M.* 3, 205).—3. Heating with $ZnCl_2$ at 160° gives a mixture of *p*-xylene hexahydride and a phenol $C_{10}H_{14}O$ apparently identical with the carvacrol obtained by the action of I on camphor (R. Schiff, *B.* 13, 1407).—4. *Nitric acid* forms bromo-nitro-camphor and camphoric acid (Armstrong, *B.* 12, 1358; R. Schiff a. Maissen, *G.* 10, 317).—5. *Phenyl-hydrazine* forms $C_{10}H_{15}(N_2PhH)(N_2PhH_2)$, [56°] (Balbiano, *G.* 17, 95, 155).

(α)-Di-bromo-camphor $C_{10}H_{14}Br_2O$. [115°]. Formed, together with the preceding, by heating bromo-camphor (1 mol.) with Br (2 mols.) for 11

hours at 130° (K. a. S.; *cf.* Swarts, *Z.* [2] 2, 205; *B.* 15, 1622). Formed also by heating (β)-di-bromo-camphor with gaseous HBr at 130° (Swarts, *B.* 15, 2135). Trimetric crystals; $a:b:c = \cdot 95:1:\cdot 52$; sl. sol. alcohol, ether, and petroleum. Less volatile with steam than the preceding.

Reactions.—1. *Sodium-amalgam* gives camphor and campholenic acid.—2. Conc. HNO_3 gives di-bromo-nitro-camphor [130°].

(β)-Di-bromo-camphor $C_{10}H_{14}Br_2O$. [61°]. Formed, together with its isomeride, by the action of Br (1 mol.) on bromo-camphor (1 mol.) for 7 hours at 120° (Kachler a. Spitzer, *M.* 3, 208; Zepharovich, *M.* 3, 231; *cf.* R. Schiff, *G.* 11, 178; Montgolfier, *Bl.* [2] 23, 253). Trimetric crystals, $a:b:c = 2\cdot 0685:1:1\cdot 5778$ (Cazeneuve a. Morel, *Bl.* [2] 44, 161) $= 1\cdot 944:1:1\cdot 558$ (K. a. S.). V. sol. alcohol, ether, and petroleum.

Reactions.—1. Alcoholic KOH, or sodium-amalgam, reduces it to bromo-camphor, and finally to camphor.—2. Sodium and CO_2 form camphor carboxylic acid.—3. Conc. HNO_3 gives camphoric, and hydro-oxy-camphoric, acids, together with bromo-di-nitro-methane (Kachler a. Spitzer, *M.* 4, 554).

(a)-Chloro-bromo-camphor $C_{10}H_{14}ClBrO$. [98°]. $[\alpha]_j = 78°$. Formed by heating chloro-camphor [84°] with bromine in sealed tubes for 5 hours at 100°. White needles. Insol. water, sol. hot alcohol, ether, and $CHCl_3$ (Cazeneuve, *Bl.* [2] 44, 115; *C. R.* 100, 802).

(β)-Chloro-bromo-camphor $C_{10}H_{14}ClBrO$. [51·5°]. $[\alpha]_j = 51°$. Prepared by heating chloro-camphor (1 mol.) with bromine (2 mols.) in sealed tubes for one hour at 100° C. Hard, trimetric crystals, $a:b:c = 1\cdot 9141:1:1\cdot 5395$. Insol. water, v. sol. alcohol, v. sol. ether, $CHCl_3$, C_6H_6 and CS_2 (Cazeneuve, *Bl.* [2] 44, 115; *C. R.* 100, 859). Decomposed by boiling AgOAcAq (difference from preceding).

Iodo-camphor $C_{10}H_{15}IO$. [44°]. Formed, together with NaCy and NaI, by the action of ICy on sodium-borneol dissolved in benzene (Haller, *C. R.* 87, 695). Monoclinic crystals, insol. water, sol. alcohol. Decomposes at about 150°.

Nitro-camphor $C_{10}H_{15}NO_3$ [83°]. Prepared by the action of alcoholic KOH on bromo-nitro-camphor (Schiff, *B.* 13, 1402; *G.* 10, 330; 11, 21). Dissolves in aqueous alkalis. Gives a red colouration with Fe_2Cl_6. HNO_2 gives a nitroso-compound. On oxidation with HNO_3 it gives camphoric acid. By reduction it gives amido-camphor. Bromine forms $C_{30}H_{43}N_3Br_2O_{11}$? [95°]. Cl forms similarly $C_{30}H_{43}N_3Cl_2O_{11}$? [110°]. Steam-distillation gives camphoric acid and anhydride and NH_3. This substance is probably a mixture of the two following.

(a)-Nitro-camphor $C_{10}H_{15}(NO_2)O$. [101°]. $[\alpha]_j$ (19·978 p.c. in benzene) $-98°$; (3·33 p.c. in alcohol) $-7\cdot 5°$. Formed, together with its (β)-isomeride, by the action of Zn, Cu, Fe, or alkalis on either chloro-nitro-camphor dissolved in alcohol. Best prepared by using the copper-zinc couple. The resulting zinc-salt of nitro-camphor is decomposed by HCl. The (a)-compound is the less soluble in cold alcohol (Cazeneuve, *C. R.* 103, 275; 104, 1522; *Bl.* [2] 47, 920). Trimetric prisms. Decomposes at 160°. Lævorotatory. Its rotation varies with concentration of the solution. It forms a compound with benzene. It reddens litmus, and decomposes carbonates. Fe_2Cl_6 colours its alcoholic solution blood-red.

(β)-Nitro-camphor $C_{10}H_{15}(NO_2)O$. [98°]. $[\alpha]_j$ (3·33 p.c. in benzene) $-75°$; (3·33 p.c. in alcohol) $+7\cdot 5°$. Prepared as above. Soft, fern-like, crystals (from alcohol). Insol. water, sol. other menstrua. Less stable than the (a)-isomeride. Fe_2Cl_6 colours its solutions red. Its salts are more soluble than those of the (a)-compound.—NaA'.—ZnA'$_2$: sol. water.

(a)-Chloro-nitro-camphor $C_{10}H_{14}Cl(NO_2)O$. [95°]. $[\alpha]_j = -6\cdot 2°$. From chloro-camphor [93°] (1 pt.) and fuming HNO_3 (4 pts.). Large trimetric prisms (from alcohol); $a:b:c = 2\cdot 022:1:1\cdot 475$ (the author does not say whether these numbers belong to this or to the following body). Insol. water, m. sol. cold alcohol. Decomposes above 100°. Reduced by nascent hydrogen to nitro-camphor (Cazeneuve, *C. R.* 96, 589; *Bl.* [2] 39, 503).

(β)-Chloro-nitro-camphor $C_{10}H_{14}Cl(NO_2)O$. [98°]. $[\alpha]_j = 10\cdot 5°$ (in alcohol). Occurs in the mother-liquor from which the preceding has separated. Soft crystals, v. sol. cold alcohol. Reduction gives nitro-camphor. Less stable than the (a)-isomeride, for alkalis remove Cl forming nitro-camphor even in the cold. Not decomposed by alcoholic $AgNO_3$ (Cazeneuve, *C. R.* 98, 306; *Bl.* [2] 41, 285; 44, 161; 47, 926).

(?)-Bromo-nitro-camphor $C_{10}H_{14}BrNO_3$. [105°]. $[\alpha]_j = -27°$. Prepared by nitration of bromo-camphor. Trimetric crystals, $a:b:c = 2\cdot 0854:1:1\cdot 5423$. Nearly insol. cold alcohol. By the action of alcoholic KOH or nascent H it gives nitro-camphor (Schiff, *G.* 10, 324; *B.* 13, 1402; 14, 1377).

Di-bromo-nitro-camphor $C_{10}H_{13}Br_2(NO_2)O$. [130°]. From (a)-di-bromo-camphor by nitration (Kachler a. Spitzer, *M.* 4, 554). Trimetric prisms or needles, $a:b:c = 1\cdot 76:1:1\cdot 49$. Reduced by tin and HOAc to amido-camphor.

Amido-camphor $C_{10}H_{17}NO$. (247°). Waxy solid. Strong base of alkaline reaction. Prepared by reduction of nitro-camphor with sodium-amalgam in alkaline solution. It reduces Fehling's solution, $AgNO_3$, and $HgCl_2$. With HNO_2 it produces oxy-camphor (Schiff, *B.* 13, 1404). On distillation of the hydrochloride of amido-camphor with steam, 'dicamphylamine' $C_{20}H_{31}NO_2$ passes over and 'camphimide' $C_{10}H_{15}N$ remains in the retort. D i c a m-p h y l a m i n e [160°] crystallises in needles, insol. acids, volatile with steam. C a m p h-i m i d e forms crystalline flakes, soluble in acids; nitrous acid converts its hydrochloride into 'diazo-camphor' $C_{10}H_{14}N_2O$ [74°] which may be reduced by Zn and HOAc to amido-camphor. Diazo-camphor is converted by heat into 'de-hydro-camphor' $C_{10}H_{14}O$ [160°] (R. Schiff, *G.* 10, 362; 11, 171; *B.* 14, 1375).

Oxy-camphor (?) $C_{10}H_{16}O_2$ [155°]. Prepared by the action of HNO_2 on amido-camphor (Schiff, *B.* 13, 1404). Colourless crystals. Volatile with steam.

Wheeler's chloro-camphor (*q.v.*) gave with alcoholic KOH an 'oxy-camphor' [137°].

The acetyl derivative [69°] of an 'oxy-camphor' [249°] is formed by oxidising acetyl-borneol.

An 'oxy-camphor' [61°] is formed by oxidising camphene (*v.* TERPENES) (Kachler a. Spitzer, *A.* 200, 358).

V. also CAMPHOLENIC ACID.

'Nitro-oxy-camphor,' *v.* NITRO-CAMPHOLENIC ACID.

Cyano-camphor *v. Nitrile of* CAMPHOR CARBOXYLIC ACID.

Ethyl-camphor $C_{10}H_{15}EtO$. (228°). S.G. $\frac{22}{}$ ·946. $[\alpha]_j = 161°$. From sodium-camphor and EtI (Baubigny, *Z.* [2] 4, 481). Oil.

Isoamyl-camphor $C_{10}H_{15}(C_5H_{11})O$. (278° cor.). $[\alpha]_j = 59·4°$. From sodium-camphor and isoamyl iodide (B.).

'Nitrohexoic acid' $C_6H_{11}(NO_2)O_2$ *i.e.* $Me.CH(NO_2).CMe_2.CO_2H$(?) [115°]. From dinitroheptoic acid and sodium-amalgam (Kullhem, *A.* 167, 45; Kachler, *A.* 191, 157). Rectangular four-sided columns (from water). Monoclinic; $b:c = 1:·6115$; $\beta = 83°\ 30'$. After several fusions it melts at 111·5°. Quickly heated, it explodes.

Reactions.—1. Dissolved in a little aqueous KOH, mixed with KNO_2 and dilute H_2SO_4 a fine blue colour is formed. This colour is taken up by ether; hence the body is probably akin to pseudo-nitroles.—2. Sn and HCl produce methyl-isopropyl ketone, hydroxylamine, and CO_2.—3. Baryta in sealed tubes at 95° does not decompose it, but forms the basic salt $C_6H_9BaNO_4$.

Dinitrohexoic acid $C_6H_{10}(NO_2)_2O_2$? *i.e.* $MeC(N_2O_4).CMe_2.CO_2H$ (?) [215°]. Got by Kullhem by treating the residues in the preparation of camphoric acid with strong HNO_3 (*A.* 163, 231; Kachler, *A.* 191, 155). Monoclinic plates; $a:b:c = ·5735:1:·6024$; $\beta = 70°\ 42'$. M. sol. cold water, v. sol. hot water. Explodes when rapidly heated. Its ammonium salt gives with cupric acetate a bluish pp. sol. excess of the acetate (difference from camphoric acid). The free acid does not pp. cupric or lead acetate. The neutral salts give a flocculent pp. with lead acetate.

Salt.—BaA'_2 3aq. Needles.

Reactions.—1. Reduced in alcoholic solution by *sodium amalgam* to mononitroheptoic acid. 2. Reduced by Sn and HCl to methyl iso-propyl ketone and hydroxylamine.—3. *Potash* and *baryta* heated with the aqueous acid in sealed tubes produce both nitro-heptoic acid and methyl isopropyl ketone.

Hydro-oxycamphoronic acid $C_9H_{14}O_6$. [164·5°] (Kachler, *A.* 191, 148). Needles. Sol. cold water. Tribasic acid. Gives no pp. with $BaCl_2$ or $CaCl_2$ and NH_3, even on boiling (difference from camphoronic acid). Cupric acetate gives no pp. until boiled when a bluish-green cupric salt is ppd. Lead acetate gives a white pp. soluble in excess. $AgNO_3$ gives a white pp. soluble in hot water.

Salts.—NH_4H_2A'''.—$CaHA'''$ 2aq.—$Ca_3A'''_2$.—$Ba_3A'''_2$.—$Cu_3A'''_2$.—Ag_3A'''.

ISOMERIDES OF CAMPHOR.

Lævorotatory camphor $C_{10}H_{16}O$. [172° cor.] (R.); [175°] (C.). (204°). S.G. $\frac{18}{}$ ·9853 (C.). $[\alpha]_j = -47°$ (C.); $-42°$ (H.). Occurs together with a terpene in the ethereal oil obtained from the leaves of fever-few, *Matricaria Parthenium* (Chautard, *C. R.* 37, 166). Apparently formed also by oxidising the lævorotatory terpene obtained by treating with alcoholic KOH the product of the action of HCl on lævorotatory oil of terpentine (Riban, *Bl.* 24, 19). Obtained also by oxidising the borneols of madder, valerian, Ngai, and Bang-Phien (Haller, *C. R.* 103, 64; 104, 66). HNO_3 gives lævorotatory camphoric acid $[\alpha]_j = -46°$. The corresponding bromo-camphor is also lævorotatory, $[\alpha]_j = -128°$.

Inactive camphor $C_{10}H_{16}O$. [173°]. Got by oxidising inactive borneol (*q. v.*) with cold HNO_3 and then adding water (Armstrong a. Tilden, *C. J.* 35, 752). Also by oxidising inactive camphene with H_2SO_4 and $K_2Cr_2O_7$. Heated with HNO_3 it forms a camphoric acid, [203°] and giving when heated alone an anhydride, [223°].

Inactive camphor *From Oil of Sage.* $C_{10}H_{16}O$. [174°]. (205° uncor.). When oil of sage is distilled, the fraction 205°–208° deposits this camphor. It apparently only differs from ordinary camphor in being inactive, for:—1. PCl_5 gives an oil which is converted by water into a wax-like solid, [80°] whence Na forms a white solid.—2. Boiled with HNO_3 (2:1) it forms inactive camphoric acid [186°].—3. Dissolved in toluene and treated with Na and CO_2 it forms inactive borneol, [200°].—4. Distilled with P_2S_5 it forms cymene (M. M. P. Muir, *C. J.* 37, 685).

'Racemic' camphor $C_{20}H_{32}O_2$ (?). [179°]. This name is given to the product of the oxidation of a mixture of equivalent quantities of lævo- and dextro- rotatory borneol, and is therefore inactive by compensation, as racemic acid is (Haller, *C. R.* 105, 66). It gives a bromo-derivative [51°] and a camphoric acid [205°]. The 'racemic' camphor, bromo-camphor, and camphoric acid were also prepared by mixture and found to be identical with the above. They differ in solubility as well as in melting-point from the active compounds. The borneol of amber, and consequently the camphor derived therefrom, appear to be a mixture of dextro- and lævo-rotatory varieties in unequal proportions.

Camphors, or bodies resembling camphor, have been found in many essential oils, *e.g.* oils of alant (p. 94), absinthe (p. 2), chamomile, eucalyptus, lavender, nutmeg, rosemary, &c. When a camphor is converted into borneol, the rotatory power of the resulting borneol varies with each operation, but the camphor regenerated by oxidising the borneol has in each case the rotatory power of the original camphor (Montgolfier). According to Haller (*C. R.* 105, 228) this may be explained by supposing that the resulting borneol is always a mixture of a stable borneol rotating in the same direction as the original camphor and of an unstable borneol rotating in the opposite direction.

CAMPHOR-CARBOXYLIC ACID $C_{11}H_{16}O_3$. [129°]. Formed as a by-product in the preparation of borneol from camphor by the action of Na on a solution of camphor in toluene, the product being treated with CO_2. It is produced by the union of CO_2 with sodium-camphor (Baubigny, *Z.* [2] 4, 481, 647; *A. Ch.* [4] 19, 221; Kachler a. Spitzer, *B.* 13, 1412; *M.* 2, 233). Long colourless monoclinic pyramids. Sol. water. Decomposes below 100° into CO_2 and camphor.

Reactions.—1. Boiling AcCl forms $C_{22}H_{30}O_4$ [196°], crystallising in needles.—2. P_2O_5, acting

on its solution in $CHCl_3$, forms $C_{22}H_{30}O_3$ [265°]. 3. PCl_5 forms $C_{22}H_{28}Cl_4$ [45°] which separates from ether-alcohol in triclinic crystals $a{:}b{:}c$ = 1:·804:·47.

Salts.—NaA'.—BaA'_2.—PbA'_2.

Ethyl ether EtA': (276° uncor.); S.G. $\frac{15}{}$ 1·052; colourless fluid (Roser, *B.* 18, 3113).

Nitrile $C_{10}H_{15}CyO$. *Cyano-camphor.* [128°]. (250°). Formed by passing cyanogen into a mixture of camphor and sodium-camphor dissolved in hot toluene; extracted by shaking with aqueous NaOH and ppg. by HOAc. Rectangular prisms (from ether); sol. alcohol, ether, and HOAc. Contains an atom of hydrogen displaceable by Na or K, forming unstable salts. Conc. HCl at 100° converts it into camphor carboxylic acid. Oxidising agents give HCy and camphoric acid. Alcoholic NaOH slowly converts it into the ether of camphor carboxylic acid (Haller, *C. R.* 87, 843; 93, 72; 102, 1477).

Chloro-camphor carboxylic acid $C_{11}H_{15}ClO_3$. Formed by passing Cl into a solution of sodium camphor, carboxylate (Schiff a. Puliti, *B.* 16, 887). Flocculent pp.; decomposes on fusion into CO_2 and chloro-camphor.

Bromo-camphor carboxylic acid $C_{11}H_{15}BrO_3$. [110°]. From camphor carboxylic acid and Br (Silva, *B.* 6, 1092). Both the acid and its salts readily decompose into CO_2 and bromo-camphor.—BaA'_2.—AgA'.

Oxy-camphor carboxylic acid $C_{11}H_{16}O_4$. [160°]. $[\alpha]_D = 59°$. Formed by boiling the nitrile of camphor carboxylic acid with aqueous KOH (Haller, *C. R.* 87, 929). Nodules (from ether).—CaA'' 6aq.—BaA'' 6aq.

CAMPHOR DICHLORIDE $C_{10}H_{16}Cl_2$. [155°]. Prepared by the action of PCl_5 on camphor in the cold: $C_{10}H_{16}O + PCl_5 = POCl_3 + C_{10}H_{16}Cl_2$ (Spitzer, *B.* 11, 363, 1819; *M.* 1, 319). Formed also by chlorinating bornyl chloride (Kachler a. Spitzer, *A.* 200, 361). Feathery trimetric needles; $a{:}b{:}c$ = ·917:1:1·686. Easily soluble in alcohol and ether. Easily splits off HCl.

CAMPHORIC ACID $C_{10}H_{16}O_4$ *i.e.*

$$C_8H_{14}(CO_2H)_2 \text{ or } \begin{array}{l} CH_2-CPr-CO_2H \\ | \qquad\quad | \\ CH_2-CMe-CO_2H \end{array} \text{ (Schiff)}$$

or $Pr.CH(CO_2H).CH_2.CH{:}CMe.CO_2H$ (W. Roser, *A.* 220, 278). Mol. w. 200. [186°]. S.G. 1·19. S. ·625 at 12°. R_∞ 83·14 (in a 1 p.c. aqueous solution) (Kanonnikoff, *J. pr.* [2] 31, 349). $[\alpha]_D = 46°$. Formed by boiling camphor or campholic acid with conc. HNO_3 (Kosegarten (1785); Laurent, *A. Ch.* 63, 207; Malaguti, *A. Ch.* 64, 151; *A.* 22, 50; Wreden, *A.* 163, 323; V. Meyer, *B.* 3, 116; Kachler, *A.* 162, 262). It is best to use the mixture of camphor and borneol obtained by the action of Na on camphor (Maissen, *G.* 10, 280). Formed also by the oxidation of chloro- or bromo- camphor with alkaline permanganate (Balbiano, *G.* 17, 240). Monoclinic crystals; the rotation in alkaline solution has been studied by Thomsen (*J. pr.* [2] 35, 157). The refractive power indicates a double union, which does not agree with Schiff's formula.

Reactions.—1. *Heat* splits it up into water and an anhydride.—2. *Water* at 180° changes it into meso-camphoric acid.—3. Fuming HCl at 200° forms C_8H_{14} and C_8H_{16} (Wreden, *A.* 187, 169).—4. Conc. HIAq at 200° gives xylene tetrahydride and hexahydride (W.).—5. By the action of $ZnCl_2$ xylene tetrahydride C_8H_{14} is produced:

$$C_8H_{14}(CO_2H)_2 = C_8H_{14} + CO_2 + CO + H_2O.$$

The same hydrocarbon is produced by the action of $ZnCl_2$ on ammonium camphoramic acid:

$$C_{10}H_{14}O_2(NH_2)(ONH_4) + ZnCl_2 + H_2O = 2NH_4Cl + ZnO + CO + CO_2 + C_8H_{14}$$

(Ballo, *B.* 12, 324).—6. The ammonium salt distilled with P_2O_5 gives a terpene $C_{20}H_{32}$ (Ballo, *A.* 197, 329). 7. Conc. H_2SO_4 forms CO and 'sulphocamphoric acid.'—8. Conc. HNO_3 gives camphoronic acid.—9. *Potash-fusion* gives pimelic acid $Pr.CH(CO_2H).CH_2.CO_2H$ and an acid $C_{10}H_{16}O_4$ (Hlasiwetz a. Grabowsky, *A.* 145, 205).—10. Distillation with *soda-lime* gives camphoric anhydride and phorone $C_9H_{14}O$ (Meyer, *B.* 3, 117). Distillation of camphorates gives similar results.

Salts.—(Kemper, *Ar. Ph.* [2] 110, 106; 117, 23). NH_4HA'' *x*aq.—$(NH_4)_2A''$.—Li_2A''.—Na_2A''.—K_2A'': deliquescent.—MgA'' $7\frac{1}{2}$aq. S. 40 at 20°.—MgA''12aq.—MgA'' $13\frac{1}{2}$aq.—$CaH_2A''_2$.—CaA'' $4\frac{1}{2}$aq.—CaA'' 7aq. — $Ca_3H_2A''_4$ 8aq. — $BaH_2A''_2$ 2aq.—BaA'' aq: needles and feathers (Kingzett, *C. J.* 45, 93).—BaA'' $4\frac{1}{2}$aq.—ZnA''.—PbA''.—CuA''.—Ag_2A''.

Ethyl-ammonium salt $(NH_3Et)_2A''$: small needles (from alcohol). Converted by PCl_5 into camphoric di-ethyl-imidine.

Mono-methyl ether $MeHA''$. [68°]. $[\alpha]_j = 51·4°$. Trimetric prisms (from ether); gives camphoric anhydride when distilled. V. sl. sol. water (Loir, *A. Ch.* [3] 38, 483).

Mono-ethyl ether $EtHA''$. S.G. $\frac{20·5}{}$ 1·095. Syrup.

Di-ethyl ether Et_2A''. (286°). S.G. $\frac{16}{}$ 1·029. Formed, together with camphoric anhydride, by the distillation of the mono-ethyl ether (Malaguti, *A. Ch.* [2] 64, 152; 70, 360; Meyer, *B.* 3, 118). Liquid. Chlorine produces a tetra-chloro- derivative $(C_5H_3Cl_2)_2A''$. S.G. $\frac{14}{}$ 1·386.

Chloride $C_{10}H_{14}O_2Cl_2$. Heavy oil, decomposing at 200° (Moitessier, *A.* 120, 252).

Anhydride $C_{10}H_{14}O_3$. [217°]. (above 270°). S.G. $\frac{20·5}{}$ 1·194. $[\alpha]_D = -7·7°$ (in benzene). Formed by heating camphoric acid or its salts (Bouillon-Lagrange, *A. Ch.* 23, 153; Laurent, *A. Ch.* 63, 207; Malaguti, *A. Ch.* 64, 151; Blumenau, *A.* 67, 119; Moneyer, *J. Ph.* [3] 45, 177). Formed also from camphoric acid by the action of (1 mol. of) PCl_5 (Gerhardt a. Chiozza, *A.* 87, 294), of conc. H_2SO_4, of Ac_2O, or of AcCl (Anschütz, *B.* 10, 1881). Long trimetric prisms (from alcohol) (Montgolfier, *A. Ch.* [5] 14, 5). V. sl. sol. water, v. sol. alcohol, v. e. sol. ether. Slowly converted by boiling water into camphoric acid. The statement of Brodie (*Pr.* 9, 361; 12, 655) that barium peroxide formed camphoric peroxide has been denied by Kingzett (*C. J.* 45, 93).

Amide $C_8H_{14}(CONH_2)_2$. Amorphous mass (Moitessier, *A.* 120, 253).

Imide $C_8H_{14}{:}C_2O_2{:}NH$. [180°] (in sealed tubes, Ballo, *A.* 197, 332). Formed by heating ammonium camphoramate at 160° (Laurent, *Compt. chim.* 1845, 147; *A.* 60, 327). Laminæ. May be distilled.

Ethylimide $C_8H_{14}{:}C_2O_2{:}NEt$. [50°]. (275°). Colourless crystals. Prepared by dis-

tilling ethylamine camphorate (Wallach a. Kamenski, *B.* 14, 164; *A.* 214, 248).

Allyl-imide $C_8H_{14}:C_2O_2:NC_3H_5$. [49°]. Formed by heating camphoric acid with allyl thiocarbimide. Insol. water, sol. alcohol and ether.

Phenyl-imide $C_8H_{14}:C_2O_2:NPh$. [116°]. Formed, together with phenyl-camphoramic acid, by warming camphoric anhydride with aniline (Gerhardt a. Laurent, *A.* 68, 35). Needles (from ether); insol. cold water.

Di-ethyl-imido-imidine $C_{14}H_{24}N_2O$ *i.e.*

$$C_8H_{14}\left\langle\begin{matrix}C=NC_2H_5\\ \quad\rangle NC_2H_5\\ C=O\end{matrix}\right.$$ (286°). S.G. $\frac{15}{}$ 1·018.

Liquid; v. sl. sol. water. Pps. salts of Cu and Fe. Prepared by the action of PCl_5 on ethylamine-camphorate or by the action of ethylamine on the chloride ($C_8H_{14}\left\langle\begin{matrix}CCl_2\\ \rangle NEt\\ CO\end{matrix}\right.$) obtained from PCl_5 and camphoric-ethyl-imide. By HCl at 200° it is decomposed into ethylamine and camphoric-ethyl-imide. Salts.—B'HCl: deliquescent crystals.—B'HI: sparingly soluble needles.—$(B'HCl)_2PtCl_4$. Its *ethylo-iodide* B'EtI: [245°]; forms long colourless prisms (Wallach a. Kamenski, *B.* 14, 162; *A.* 214, 242).

Nitrile $C_8H_{14}(CN)_2$. Formed, in small quantity, together with hydrocarbons C_8H_{14} and $C_{20}H_{32}$ by distilling ammonium camphoramate with P_2O_5 (Ballo, *A.* 197, 334). Crystalline; insol. water.

Camphoramic acid $C_8H_{14}(CONH_2)(CO_2H)$. So-called '*amido-camphoric acid*.' The ammonium salt is formed by the action of NH_3 on an alcoholic solution of camphoric anhydride (Laurent, *Compt. chim.* 1845, 147; *A.* 60, 326). Trimetric crystals; m. sol. hot water, v. sol. alcohol.—NH_4A' aq. [?200°]. When heated with dry $ZnCl_2$ it gives xylene tetrahydride and a terpene (Ballo, *B.* 12, 324).—PbA'_2.—AgA'.

Phenyl-camphoramic acid

$C_8H_{14}(CONPhH)(CO_2H)$. Formed by boiling the phenyl-imide of camphoric acid with alcoholic NH_3, or camphoric anhydride with aniline. Needles (from alcohol); v. sl. sol. boiling water. —AgA' (Laurent a. Gerhardt, *A.* 68, 36).

Bromo-camphoric anhydride

$C_8H_{13}Br\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$. From camphoric anhydride (10 g.) and Br (15 g.) at 130° (Woringer, *A.* 227, 3); an additive compound $C_{10}H_{14}O_3Br_2$ appears to be first formed (Wreden, *A.* 163, 330). Trimetric crystals (from chloroform). $a:b:c$ = ·8866:1:·5766. NH_3 gives the imide of oxy-camphoric acid.

(α)-Oxy-camphoric acid $C_{10}H_{16}O_5$. Formed, together with pimelic acid, by fusing camphor with KOH (Hlasiwetz a. Grabowski, *A.* 145, 212). Thick liquid; the salts are amorphous.

(β)-Oxy-camphoric acid $C_{10}H_{16}O_5$

Anhydride $C_{10}H_{14}O_4$ *i.e.*

$C_8H_{13}(OH):C_2O_2:O$ (?) *Camphanic acid.* [201°]. Formed by boiling bromo-camphoric anhydride with water (Kachler, *A.* 162, 264). Monoclinic prisms (containing aq or 2aq) (Grünling, *A.* 227, 4). Sublimes at 110°. Decomposed on distillation giving CO_2, lauronolic acid $C_9H_{14}O_2$, and 'campho-lactone' $C_9H_{14}O_2$. Water at 180° splits it up into CO_2 and C_8H_{14} (119°).—$Ba(C_{10}H_{13}O_4)_2$ $1\frac{1}{2}$aq.—$Cd(C_{10}H_{13}O_4)_2$ 3aq.

Ethyl ether $EtC_{10}H_{13}O_4$. [63°]. From bromo-camphoric anhydride and alcohol at 150°. Prisms.

Imide $C_{10}H_{15}NO_3$ *i.e.* $C_8H_{13}(OH):C_2O_2:NH$ (?) [208°]. *Amido-camphoric anhydride.* From bromo-camphoric anhydride and conc. NH_3Aq at 150° (Wreden, *A.* 163, 339). Long needles (from alcohol). Sublimes at 150°. Converted by nitrous acid into the anhydride.

Oxy-camphoramic acid $C_{10}H_{17}NO_4$ *i.e.* $C_8H_{13}(OH)(CONH_2)(CO_2H)$. '*Amido-camphoric acid.*' [160°]. Formed by boiling the imide of oxy-camphoric acid with dilute KOH (Wreden, *A.* 163, 340). Prisms containing aq (from alcohol). On fusion it is converted into the parent imide. Converted into oxy-camphoric anhydride by HNO_2, by conc. HClAq, or by H_2SO_4.—CaA'_2 2aq.

'Sulpho-camphoric acid' so-called. $C_9H_{16}SO_6$. [160°–165°]. *Sulphocamphylic acid.* Formed, together with CO, by heating camphoric acid or anhydride with conc. H_2SO_4 (Walter, *A. Ch.* [3] 9, 177; Kachler, *A.* 169, 179). Triclinic prisms (containing 2aq); $a:b:c$ = ·8515:1:·7590; α = 82° 39′; β = 121° 10′; γ = 111° 36′ (Zepharovich, *Sitz. B.* 73, 7). V. e. sol. water, alcohol, and ether. HNO_3 (S.G. 1·25) converts it into $C_7H_{12}SO_7$. Potash-fusion gives $C_9H_{12}O_2$ [148°], insol. cold water, but separating from alcohol in monoclinic crystals.

Salts.—$(NH_4)_2A''$ aq.—K_2A''.—CaA''.—BaA''.—$PbH_2A''_2$ 4aq: trimetric.—PbA''.—$BaCuA''_2$.—Ag_2A''.

ISOMERIDES OF CAMPHORIC ACID.

Lævo-rotatory camphoric acid $C_{10}H_{16}O_4$. [186°]. $[\alpha]_j = -46·3°$ (in alcohol). Formed by the oxidation of lævo-rotatory ($[\alpha]_j = -38°$) borneol, or the corresponding camphor, by heating for several hours with a large excess of HNO_3 (S.G. 1·27) (Chautard, *C. R.* 37, 166; Haller, *C. R.* 103, 64). Resembles camphoric acid in all respects except that its rotation though equal is opposite.

Inactive camphoric acid $(C_{10}H_{16}O_4)_2$. [204°]. S. 1; S. (alcohol) 33; S. (ether) 28 (C.). Formed by heating inactive camphor with HNO_3 at 100°, or by mixing equal weights of dextro- and lævo-camphoric acids (Chautard, *C. R.* 56, 698; Armstrong a. Tilden, *C. J.* 35, 757; Haller, *C. R.* 105, 66). Less soluble than its isomerides.

Diethyl ether Et_2A''. (270°–275°). S.G. $\frac{15}{}$ 1·03 (C.).

Anhydride $(C_{10}H_{14}O_3)_2$. [223°] (A. a. T.). S. (chloroform) 25; S. (ether) 4; S. (alcohol) 1·5 (C.). Formed by heating the acid.

An inactive camphoric acid [186°] was obtained by Muir (*C. J.* 37, 685) by oxidising the camphor of oil of sage.

Meso-camphoric acid $C_{10}H_{16}O_4$. [113°].

Formation.—1. Formed by heating dextro-camphoric acid (5 g.) with (20 c.c.) fuming HCl at 140° for 30 hours (Wreden, *Z.* [2] 7, 419; *A.* 163, 328; *B.* 6, 565).—2. By heating dextro-camphoric acid (5 g.) with HI (30 c.c. of S.G. 1·6) at 160°.—3. By heating camphoric acid with water at 200° (Jungfleisch, *B.* 6, 268, 680). 4. Together with 'sulphocamphoric acid' by the

action of H_2SO_4 on camphor. Occurs also in small quantity in the preparation of camphoric acid from camphor and HNO_3 (Kachler, *A.* 169, 179; 191, 146).

Properties.—Crystalline, but separates from alcohol and ether as an oil. More soluble than ordinary camphoric acid. Conc. H_2SO_4 converts it on warming into 'sulphocamphoric acid.' When heated it gives the anhydride of ordinary camphoric acid. Boiling dilute HCl changes it into inactive camphoric acid.

CAMPHORIDE $C_{16}H_{12}O_6$. [222°]. Occurs together with galangin and alpinin in the galanga root (*Alpinia officinarum*). Flat yellow needles (containing aq), sublimable. Sol. hot alcohol, ether, and acetic acid, sl. sol. chloroform and benzene, insol. water. Dissolves in alkalis. On oxidation with dilute HNO_3 it produces anisic and oxalic acids.

Salts.—A″Pb: yellow amorphous pp.—$A''Pb_2O$.—A″Ba 2aq: orange pp.

Di-acetyl derivative $C_{16}H_{10}O_4(OAc)_2$. [189°]. Colourless crystals. Insol. water. Sl. sol. alcohol.

Di-benzoyl derivative $C_{16}H_{10}O_4(OBz)_2$. [186°]. Fine white needles. Scarcely sol. alcohol, insol. water.

Di-bromo-derivative $C_{16}H_{10}Br_2O_6$. [225°]. Yellow needles. Sl. sol. alcohol (Jahns, *B.* 14, 2385).

CAMPHOR-IMIDO-ACETIC ETHER

$C_{14}H_{21}NO_4$ *i.e.* $C_8H_{14}<\begin{smallmatrix}CO\\CO\end{smallmatrix}>N.CH_2.CO_2Et$. [86°]. Formed by adding a solution of $CH_2Cl.CO_2Et$ to a solution of sodio-camphorimide in absolute alcohol. Large transparent crystals (from alcohol), sol. ether (Haller a. Arth, *C. R.* 105, 281).

CAMPHOR OIL. An oil obtained, together with camphor, by distilling the wood of *Laurus camphora* with water. It consists chiefly of 'camphorogenol' but contains also several terpenes (*q. v.*).

Camphorogenol $C_{10}H_{16}O_2$ or $C_{10}H_{18}O_2$ or $C_{10}H_{16}Oaq$ (?) S.G. $\frac{20}{}$ ·9794. $[\alpha]_j = 29·6°$. An oil, v. e. sol. alcohol and ether. HNO_3 acts upon it forming a small quantity of camphor. CrO_3 acts similarly. Excess of conc. HNO_3 gives camphoric acid [185°], $[\alpha]_j = 40·3°$. Ac_2O has no action. Sodium reduces it, in alcoholic solution, to borneol, [198°], (212°), $[\alpha]_j = 22·9°$. With $ZnCl_2$ it yields cymene (Yoshida, *C. J.* 47, 785; Oishi, *C. N.* 50, 275; Wallach, *A.* 227, 296; Lallemand, *A. Ch.* [3] 57, 404).

CAMPHOR-PHORONE *v.* Phorone.

CAMPHORONIC ACID $C_9H_{14}O_6$. Mol. w. 218. [137°] Formed by oxidising campholic or camphanic acids (Bredt, *B.* 18, 2989).

Preparation.—From camphor and HNO_3. Present in the mother liquor from which camphoric acid has separated. Obtained by means of the barium salt (Kachler) and purified by decomposing this with HCl, extracting with ether, boiling off the ether, dissolving in water, neutralising with lime and boiling. The pure calcium salt then separates (Bredt, *A.* 226, 251; *cf.* Kachler, *B.* 7, 1728; *A.* 159, 286; 162, 262; Kachler a. Spitzer, *M.* 6, 173).

Properties.—Crystalline aggregates of needles, v. e. sol. water, alcohol, and wet ether, sl. sol. pure ether. Produces on distillation CO_2, isobutyric acid and the anhydride $C_9H_{12}O_5$ [135°] which forms trimetric crystals, $a:b:c = ·96:1:·82$; sol. water, alcohol and ether. This anhydride forms with NH_3 the compound $C_9H_{11}(NH_4)O_6$ [c. 128°], v. sol. water.

Reactions.—1. AcCl gives $C_9H_{12}O_5$ and then the anhydride $C_{18}H_{22}O_9$ [176°]; crystals, insol. cold alcohol and ether; reconverted into camphoronic acid by boiling alkalis.—2. Br at 130° gives oxy-camphoronic acid.—3. *Potash-fusion* gives isobutyric acid.—4. *Aqua-regia* forms two acids $C_9H_{12}O_6$.—5. $KMnO_4$ gives HOAc and an acid $C_8H_{12}O_4$ (Kachler, *M.* 5, 415).—6. The Ca salt distilled with lime gives a ketone $C_7H_{12}O$.

Salts.—NH_4H_2A''': [128°].—$(NH_4)_2HA'''$: [148°].—K_2HO''' aq.—$Ca_3A'''_2$ 12aq.—BaHA‴aq: m.sol. water.—$Ba_3A'''_2$: insol. water.—$Ba_3A'''_2$ 6aq.—$Ba_3A'''_2$ 10aq.—ZnHA‴: v. e. sol. water.—CdHA‴ 6aq. — $Pb_3A'''_2$ 4aq. — $Cu_3A'''_2$ 2aq. — CuHA‴ $2\frac{1}{2}$aq.—$Cu_3A'''_2$.—Ag_3A'''.—Ag_2HA'''aq.

Mono-ethyl ether.—The anhydride (302°) (or anhydrides liquid and solid [67°], Hjelt, *B.* 13, 797) $C_9H_{11}EtO_5$ of this ether is formed together with alcohol by distilling the di-ethyl ether.

Di-ethyl ether Et_2HA'''. From the acid, alcohol, and HCl.

Tri-ethyl ether Et_3A'''. (302°). From Ag_3A''' and EtI. Liquid.

Chloride $C_9H_{11}OCl$. [131°]. Needles, sl. sol. water, sol. alcohol and ether.

Mono-amic acid $C_6H_{11}(CONH_2)(CO_2H)_2$.

Anhydride $C_9H_{13}NO_4$. [212°]. From liquid *mono-ethyl* camphoronate and alcoholic NH_3 (Hjelt, *B.* 13, 798). By the same treatment the solid ethyl camphoronate gives a compound $C_9H_{16}N_2O_4$ (? di-amic acid) crystallising with HOEt. It melts at [145°], and is converted by boiling HClAq into camphoronic acid.

Di-amic acid $C_9H_{16}N_2O_4$ *i.e.* $C_6H_{11}(CONH_2)_2(CO_2H)$. [c. 160°]. From di-ethyl camphoronate and NH_3 at 120° (H.). HClAq converts it into a compound $C_9H_{13}NO_4$ [212°].

Constitution.—Camphoronic acid appears to contain 3 carboxyls: $C_6H_{11}(CO_2H)_3$, as shown by the salts and ethers. AcCl gives no acetyl derivative. The formation of an anhydride by distilling the ether does not prove it to be lactonic. Potash-fusion produces iso-butyric acid, hence it contains isopropyl. Since it does not split off CO_2 on distillation, the carboxyls must be attached to different carbon atoms. Hence it is isopropyl-tri-carballylic acid,

$CH_2(CO_2H).CPr(CO_2H).CH_2.CO_2H$ or
$CH_2(CO_2H).CH(CO_2H).CHPr.CO_2H$.

Oxy-camphoronic acid $C_9H_{12}O_6$. [c. 210°]. Formed by heating camphoronic acid $C_9H_{14}O_6$ (1 mol.) with Br (1 mol.) for two hours at 130° (Kachler, *A.* 159, 296). Monoclinic crystals (containing aq), $a:b:c = 1·4918:1:·9808$; $\beta = 86° 50'$. According to Zepharovich (*J.* 1877, 641) they are dimorphous. V. sol. water, alcohol, and ether; may be distilled.

Salts.—KHA″aq. crystals.—K_2A'': gummy.—BaA″ aq: pearly plates.—$Pb_3(C_9H_9O_6)_2$ 2aq.—Ag_2A''.

Hydro-oxy-camphoronic acid *v.* Camphor.

CAMPHOROXIM $C_{10}H_{17}NO$ *i.e.* $C_{10}H_{16}$:N.OH. [115°]. (c. 250°). Formed by the action of hydroxylamine on camphor (Nägeli, *B.* 16, 498).

Long needles. Smells like camphor and rotates on water. Sol. alcohol, ether, acids and alkalis.

Reactions.—1. Hydroxylamine is not split off by heating with aqueous HCl even at 120°.—2. By heating with acetyl chloride it loses H_2O yielding the nitrile of campholenic acid $C_{10}H_{15}N$ (Goldschmidt a. Zürrer, *B.* 17, 2069).—3. Is reduced in alcoholic solution by metallic sodium to bornylamine $C_8H_{14}\left<\begin{array}{l}CH_2\\ |\\ CH.NH_2\end{array}\right.$. The oxim-anhydride is reduced to the isomeric camphylamine (Leuchart a. Bach, *B.* 20, 111).

Hydrochloride $C_{10}H_{16}NOH,HCl$: white powder, sl. sol. water, v. sol. alcohol and acids.

Sodium salt.—$C_{10}H_{16}N(ONa)$: white powder, v. sol. hot water and hot alcohol.

Ethyl ether $C_{10}H_{16}N(OEt)$: (209°); mobile liquid.

Anhydride $C_{10}H_{15}N$: (217°), liquid; formed by heating camphoroxim with acetyl chloride. Is the *nitrile* of Campholenic acid (*q. v.*) (Nägeli, *B.* 16, 2981).

Isocamphor-oxim is the *amide* of Campholenic acid (*q. v.*).

CAMPHO-TERPENE *v.* Terpenes.

CAMPHRENE *v.* Phorone.

CAMPHRESIC ACID or **CAMPHRETIC ACID** so called by Schwanert (*A.* 128, 77) has been shown by Kachler (*A.* 191, 143) to be a mixture of camphoric and camphoronic acids.

CAMPHYLAMINE $C_{10}H_{19}N$ possibly $C_8H_{13}(CH_2NH_2):CH_2$ (195°). Prepared by adding metallic sodium to an alcoholic solution of campholenic nitrile (camphor-oxim-anhydride). Colourless liquid. Volatile with steam. Readily absorbs CO_2 from the air and solidifies to a crystalline carbonate. Primary base.

Salts.—$B'_2H_2Cl_2PtCl_4$: glistening golden plates, nearly insol. water.—$B'HClHgCl_2$: colourless orthorhombic plates; sol. hot water.—$B'C_2H_2O_4\frac{1}{2}aq$: [194°], colourless orthorhombic glistening crystals, v. sol. hot water.—$B'_2H_2SO_4aq$: long rhombic prisms, m sol. cold water.—$B'_2H_2Cr_2O_7$: orange-red plates.—The *picrate* forms fine yellow needles, [190°–194°].

Benzoyl derivative $C_{10}H_{18}NBz$: [77°], colourless prisms (Goldschmidt a. Schulhof, *B.* 18, 3297; 19, 708; 20, 483).

Isomeride *v.* Bornylamine.

CAMPHYL-PHENYL-THIO-UREA $SC(NHC_6H_5)(NHC_{10}H_{17})$. [118°]. Formed by combination of phenyl-thiocarbimide and camphylamine. Short colourless prisms. V. sol. alcohol and benzene, sl. sol. ether, v. sol. ligroïn (Goldschmidt a. Schulhof, *B.* 19, 712).

CAMPHYL-DI-THIO-CARBAMIC ACID $C_{10}H_{17}.NH.CS.SH$. The camphylamine salt, $C_{10}H_{17}.NH.CS.SNH_3(C_{10}H_{17})$, is formed by mixing camphylamine with CS_2. White powder, [110°–116°], sol. benzene. The sodium salt $C_{10}H_{17}.NH.CS.SNa$ forms white glistening plates, sol. cold, decomposed by hot, water (Goldschmidt, *B.* 19, 712).

CANADA BALSAM. Exudes from incisions in the bark of *Abies balsamea*. Transparent thick liquid with refractive index (1·532) nearly the same as that of crown glass. Dextrorotatory. Steam-distillation separates a lævorotatory terpene (167°), which forms a crystalline compound with HCl (Donastre, *J. Ph.* 8, 572; Caillot, *J. Ph.* 16, 436; Wirzen, *Dissertation*, Helsingfors, 1849).

CANADOL. A term applied by Vohl (*D. P. J.* 172, 319) to that portion of the volatile hydrocarbons of Canadian and Pennsylvanian petroleum which boils at 60° and has a S.G. ·65 to ·70. It is also called petroleum-ether or ligroïn. It consists chiefly of *n*-hexane.

CANANGA OIL. *Alan-gilan.* From *Cananga odorata.* Neutral oil (170°–290°). It contains benzoyl and acetyl derivatives, a compound that unites with $NaHSO_3$, and probably a phenol (Flückiger, *Ph.* [3] 11, 934).

CANARIUM. The fixed oil of *Canarium commune* contains 51 p.c. oleïn and 49 p.c. stearin and myristin (Oudemans, *J. pr.* 99, 407).

CANAÜBA WAX *v.* Carnaüba wax.

CANE SUGAR *v.* Sugar.

CANNABIS INDICA. Indian hemp when distilled with steam yields an essential oil $C_{15}H_{24}$ (257°); V.D. 7·1; S.G. $\frac{0}{0}$ ·93; $[\alpha]_D = -10{\cdot}81$ at 25·5° (in chloroform). The oil resinifies on exposure (Valenta, *G.* 10, 479; 11, 196; *cf.* Martius, *C. C.* 1856, 225; Personne, *J. Ph.* [3] 31, 46). HNO_3 (S.G. 1·32 to 1·42) acting on the resinous extract of Indian hemp forms 'oxy-cannabene' $C_{20}H_{20}N_2O_7$ (Bolas a. Francis, *C. J.* 22, 417; *C. N.* 24, 77). This separates from methylated spirit in flat yellow prisms [176°], insol. water, sl. sol. alcohol. Indian hemp, and its alcoholic extract, contain a poisonous resin (T. a. H. Smith, *Ph.* 6, 127, 171; Martius). Hay (*Ph.* [3] 13, 998) has extracted a crystalline alkaloid 'tetano-cannabine' which produces tetanus in frogs. The fixed oil from hemp-seed (*Cannabis sativa*) is probably a fatty oil, though Lefort (*C. R.* 35, 734) gives it the formula $C_{11}H_{22}O_2$ and describes $C_{11}H_{20}Cl_2O_2$ and $C_{11}H_{20}Br_2O_2$ as products of substitution.

CANNON-METAL *v.* Copper, alloys of.

CANTHARENE C_8H_{12} *i.e.* $C_6H_6(CH_3)_2$ [1:2]. (134°). *o-Xylene-di-hydride.*

Formation.—1. By heating cantharic acid with fused KOH.—2. By heating cantharic acid or cantharidin with water at 300°, CO_2 being split off.—3. In a pure state by boiling with conc. aqueous KOH, the product $C_{10}H_{12}O_3I_2$, obtained together with cantharic acid by the action of HI upon cantharidine (Piccard, *B.* 12, 577; 19, 1404).

Properties.—Liquid, smelling like turpentine and camphor. Absorbs oxygen with avidity. Dilute HNO_3 oxidises it to *o*-toluic and phthalic acids.

CANTHARIC ACID $C_{10}H_{12}O_4$ *i.e.* $(C_8H_{11}O)CO.CO_2H$. [278° cor.]. S. 85 at 15°; 8·5 at 100°. Prepared by heating 1 pt. of cantharidine with 4 pts. of HI (1·96 S.G.) for $2\frac{1}{2}$ hours at 100°. Trimetric crystals (from water); v. e. sol. alcohol, v. sl. sol. ether. Distilled with lime it gives cantharene, a little xylene, butyric acid, and di-methyl-benzoic acid. It is an α-ketonic acid, for on heating with di-methyl-aniline and $ZnCl_2$ it evolves CO_2 and yields a condensation product $C_{25}H_{32}ON_2$; the latter is converted into a green colouring-matter by MnO_2, into a violet colouring-matter by chloranil or arsenic acid.—A'Ag: white pp.—KA': slender needles.—PbA'_2xaq.

Methyl ether A'Me: (210°–220°) at 50 mm.; colourless liquid.

Ethyl ether A'Et (c. 300°).

Oxim $C_{10}H_{12}O_3(NOH)$: [175°-180°]; colourless four-sided plates (Piccard, *B.* 10, 1504; 11, 2121; Homolka, *B.* 19, 1086).

CANTHARIDIC ACID $C_{10}H_{14}O_5$ *i.e.* $(C_8H_{13}O_2).CO.CO_2H$. The alkaline salts are formed by heating cantharidin with aqueous alkalis. When a cold solution of the salts is treated with acids, the free cantharidic acid appears to be formed, but on warming the solution it loses H_2O and cantharidin is precipitated. With hydroxylamine it gives an *oxim*, from the salts of which acids liberate the oxim of cantharidine.—Ag_2A''aq.—Ag_2A''2aq. $(NH_4)_2A''$aq. -K_2A''aq.—CdA''aq.—$K_2CuA''_2$2aq.

Di-methyl ether $A''Me_2$: [91°]; large flat glistening prisms; sol. alcohol, ether, and hot water, sl. sol. cold water (Homolka, *B.* 19, 1082; Dragendorff a. Masing, *Z.* 1867, 464; Masing, *J.* 1872, 841).

CANTHARIDIN $C_{10}H_{12}O_4$. *Lactone of cantharidic acid.* [218° cor.]. S. ·02 at 15°; ·29 at 100°; S. (alcohol) 2·1 at 78°; ·13 at 15°; S. (benzene) 3·38 at 80°, ·51 at 15° (Rennard); S. (ether) ·11 at 18°; S. (CS_2) ·06 at 18°; S. $(CHCl_3)$ 1·2 at 18° (Bluhm).

Occurrence.—In Spanish flies (*Lytta vesicatoria*) and many other insects (Thierry, *A.* 15, 315; *J. Ph.* 21, 44; Robiquet, *A. Ch.* 76, 302; Gössmann, *A.* 86, 317; Pocklington, *Ph.* [3] 3, 681; Regnault, *A. Ch.* [2] 68, 159; Warner, *Am. J. Ph.* 28, 193; Ferrer, *J.* 1860, 597; Mortreux, *J. Ph.* [3] 46, 33; Fumouze, *J. Ph.* [4] 6, 161; Bluhm, *Z.* [2] 1, 675; Dragendorff, *Z.* [2] 3, 187, 464; 4, 308; Rennard, *C. C.* 1872, 568; Wolff, *Ar. Ph.* [3] 10, 22; Piccard, *B.* 10, 1504).

Preparation.—1. Powdered cantharides are extracted with chloroform or ether, the solvent is evaporated and the residue freed from fat by washing with CS_2.—2. Cantharides are mixed with water and MgO, dried, treated with dilute H_2SO_4 and then shaken with ether.

Properties.—Trimetric plates. Blisters the skin. Sublimes readily at 85° (Blyth).

Reactions.—1. HI forms cantharic acid.—2. By distillation with P_2S_5 it gives *o*-xylene (Piccard, *B.* 12, 580).—3. By heating with alkalis it is converted into salts of cantharidic acid $C_{10}H_{14}O_5$, from whose hot solutions cantharidin is re-precipitated on the addition of acids.

Oxim $C_{10}H_{12}O_3(NOH)$: [166°]; splendid long glistening prisms; v. e. sol. alcohol and ether, v. sol. hot water, sl. sol. cold. By conc. HCl at 150° it is split up into its constituents. — $C_{10}H_{12}O_3(NOAg)$: four-sided prisms.— $C_{10}H_{12}O_3(NOMe)$: [134°]; large colourless prisms; v. e. sol. alcohol and ether, v. sol. hot, sl. sol. cold, water (Homolka, *B.* 19, 1082).

Compound $C_{10}H_{12}O_3I_2$. '*Cantharidin iodide*' is formed as a by-product (5-8 p.c.) in the preparation of cantharic acid by the action of HI (1·96 S.G.) upon cantharidin at 85°. Crystalline solid. V. sol. benzene and chloroform, sl. sol. alcohol, insol. water. On boiling with conc. KOH it is converted into pure cantharene (*o*-xylene-di-hydride) $C_6H_6(CH_3)_2$ (Piccard, *B.* 19, 1404).

CAOUTCHOUC. *India rubber.* This substance is obtained from the milky sap of various trees belonging to several natural orders. The sap, which is obtained by making an incision in the bark of the tree, is a white creamy liquid with a sp. gr. 1·012.

The caoutchouc exists in the sap in the form of minute globules, and is consolidated in various ways, often by heating over a smoky fire which produces the brown colour of the commercial article.

Caoutchouc is colourless when pure, it is a bad conductor of heat and a non-conductor of electricity. S.G. about ·925. At ordinary temperatures it is soft, flexible, and very elastic, but at about 10° it begins to lose its elasticity, and at 0° becomes hard and rigid. When heated it loses its elasticity and becomes soft, slowly resuming its original properties when cooled; if heated to 150°-200° it melts, and after this it remains semi-liquid and sticky on cooling. It burns readily with a smoky flame, leaving little or no ash.

Exposure to air in the absence of light produces little effect on caoutchouc, but light and air together cause it to lose its elasticity and become glutinous, due to the absorption of oxygen (Spiller, *C. J.* 18, 44; Miller, *ibid.* p. 273).

Caoutchouc is insoluble in water, but when immersed in it becomes white and increases in bulk, absorbing about 25 p.c. of its weight of water, which is given up again on exposure to air. Alcohol acts upon it in a similar way.

Dilute acids do not affect it, but it is attacked by strong nitric or sulphuric acid. Chlorine renders it hard and brittle. Alkalis produce little effect.

Ether, benzene, mineral oil, sulphide of carbon, chloroform, oil of turpentine, oil of caoutchouc, and many essential and fixed oils, act upon caoutchouc, causing it to swell greatly and become gelatinous and soft. The action of these solvents appears to be to dissolve one constituent part of the caoutchouc, leaving the less soluble part in a disintegrated condition.

According to Payen, sulphide of carbon with about 5 p.c. of absolute alcohol is the best solvent.

Caoutchouc is composed of carbon and hydrogen. The proportions vary in different analyses C. 86·1 – 90·6 p.c.; H. 10 – 12·8 p.c. It appears to consist chiefly of two hydrocarbons, which can be partly separated by the prolonged action of a solvent, but the proportion of these constituents obtained varies according to the solvent employed. The more soluble part is soft and ductile, while the less soluble is tenacious and elastic.

When caoutchouc is subjected to dry distillation an oil consisting of a mixture of various hydrocarbons is obtained. This is called oil of caoutchouc.

Among the constituents of this oil are isoprene C_5H_8 (37°-38°) S.G. ·682; caoutchene $C_{10}H_{16}$ (171°) S.G. ·842, and heveene (315°) S.G. ·921 (Himly, *A. Ch.* 27, 41; Gregory, *ibid.* 16, 61; G. Williams, *Pr.* 10, 517; Bouchardat, *J. Ph.* 1837, 454; *Bl.* 24, 108; *C. R.* 89, 361).

When isoprene is acted on by strong hydric chloride a mixture of the mono- and di- hydrochlorides, together with a solid substance, is obtained. This latter is identical in its proper-

ties with caoutchouc (Bouchardat, *C. R.* 89, 1117).

Vulcanised caoutchouc.—When caoutchouc is heated to about 115° in contact with sulphur, it absorbs some of the latter and becomes vulcanised. The introduction of the sulphur can be attained in many ways, immersion in a mixture of carbon disulphide and chloride of sulphur, or in a solution of polysulphide of calcium, &c.

About 2 p.c. of sulphur appears to enter into combination with the caoutchouc. If more than this quantity is introduced the excess remains mixed with the rubber and can be dissolved out by the ordinary solvents of sulphur, while the combined sulphur cannot be so extracted. An excess of sulphur renders the caoutchouc less durable. Vulcanised caoutchouc does not lose its elasticity at a low temperature and does not soften so easily with heat as ordinary rubber. It is less affected by solvents than pure caoutchouc.

The ordinary vulcanised rubber, besides containing an excess of sulphur, is often adulterated with 40–60 p.c. of mineral matter.

Ebonite.—When caoutchouc is heated with half its weight of sulphur, with or without the addition of some mineral matter, a hard dark substance which can be polished is obtained. This is much used for insulating purposes, but according to Wright (*Am. S.* [3] 4, 29) it becomes hygroscopic when exposed to the action of ozone owing to the formation of H_2SO_4. Ebonite is little affected by the solvents of caoutchouc.

C. J. W.

CAPILLARITY *v.* PHYSICAL METHODS, *Sect.* MISCELLANEOUS.

CAPRAMIDE the *Amide* of DECOIC ACID (*q.v.*). The name has also been applied to the *amides* of OCTOIC ACID (*q.v.*) and HEXOIC ACID (*q.v.*).

CAPRAMIDOXIM *v.* HEXAMIDOXIM.

CAPRIC ACID *v.* DECOIC ACID.

CAPRIC ALDEHYDE *v.* DECOIC ALDEHYDE.

CAPRILAMIDE *v. Amide* of OCTOIC ACID.

CAPRILIC ACID *v.* OCTOIC ACID.

CAPRILONE *v.* DI-HEPTYL-KETONE.

CAPRILONITRILE *v. Nitrile* of OCTOIC ACID.

CAPRINONE *v.* DI-ENNYL-KETONE.

CAPRO-AMIDE *v. Amide* of HEXOIC ACID.

CAPRO-ANILIDE *v. Anilide* of HEXOIC ACID.

CAPROIC ACID *v.* HEXOIC ACID.

CAPROIC ALDEHYDE *v.* HEXOIC ALDEHYDE.

CAPRO-LACTONE *v. Lactone* of OXY-HEXOIC ACID.

CAPRONE *v.* DI-AMYL-KETONE.

CAPRONITRILE *v. Nitrile* of HEXOIC ACID.

CAPROYL = HEXOYL.

CAPROYL AMIDE *v. Amide* of HEXOIC ACID.

CAPROYL CHLORIDE *v. Chloride* of HEXOIC ACID.

CAPRYL ALCOHOL *v.* OCTYL ALCOHOL.

CAPRYL-AMIDE *v. Amide* of OCTOIC ACID.

CAPRYLAMINE *v.* OCTYLAMINE.

CAPRYL CHLORIDE *v. Chloride* of DECOIC ACID; also OCTYL CHLORIDE.

CAPRYL-BENZENE *v.* OCTYL-BENZENE.

CAPRYLENE *v.* OCTYLENE.

CAPRYLENE HYDRATE *v.* OCTYL ALCOHOL.

CAPRYLIC ACID *v.* OCTOIC ACID.

CAPRYLIC ALCOHOL *v.* OCTYL ALCOHOL.

CAPRYLIC ALDEHYDE *v.* OCTOIC ALDEHYDE.

CAPRYLIDENE *v.* OCTINENE.

Caprylidene tetrabromide *v.* TETRA-BROMO-OCTANE.

CAPRYLONE *v.* DI-HEPTYL-KETONE.

CAPRYLONITRILE *v. Nitrile* of OCTOIC ACID.

CAPRYL-PHENYL-AMINE *v. p*-AMIDO-PHENYL OCTANE, p. 178.

CAPSAICIN $C_9H_{14}O_2$. [59°].

Preparation. — Powdered cayenne pepper (*Capsicum fastigiatum*) is extracted with ether, the extract is evaporated, dissolved in hot alcoholic KOH, diluted with water, ppd. by $BaCl_2$, and the dried pp. treated with ether. On evaporating the extract, an oily red liquid remains, which is dissolved in dilute potash, and ppd. by addition of ammonium chloride.

Properties.—Colourless prismatic crystals, insol. water, sol. alcohol. Begins to volatilise at 100°. Powerful irritant. The pungent taste is removed by heating with potassium bichromate and dilute sulphuric acid. $BaCl_2$ and $CaCl_2$ in alcoholic solution give a pp. sol. ether; $AgNO_3$ a pp. sol. ammonia; Fe_2Cl_6 a red pp. when warmed (Thresh, *Ph.* [3] 7, 21, 259, 473).

CAPSICINE. An alkaloid which may be extracted by benzene from the fruit of *Capsicum fastigiatum.* The benzene is evaporated, and the residue dissolved in ether, from which the alkaloid is obtained by shaking with dilute H_2SO_4 (Thresh, *Ph.* [3] 6, 941). Needles; insol. water, v. sol. alcohol and ether; may be sublimed. Volatile with steam. It is not pungent. The hydrochloride crystallises in cubes and tetrahedra, the sulphate in prisms.

CAPSULÆSCIC ACID $C_{13}H_{12}O_8$. An acid obtained from the husks of the horse-chestnut (Rochleder, *Z.* 1867, 83). Crystals; may be sublimed. Fe_2Cl_6 turns its solution greenish-blue.

CARAGHEEN MOSS. *Irish pearl moss.* A gelatinous seaweed (*Chondrus crispus*). Swells up in cold water, almost entirely dissolves in hot water. Ppd. by $Pb(OAc)_2$. Appears to be chiefly composed of a carbohydrate, which is insol. Schweizer's solution, and not turned blue by H_2SO_4 and I (Schmidt, *A.* 51, 56; Flückiger a. Obermayer, *N. R. P.* 1868, 350). Caragheen moss gives galactose when boiled with dilute H_2SO_4 (Haedicke, Bauer, a. Tollens, *A.* 238, 302).

CARAJURA. A red dye, probably identical with chica red. Insol. water, sol. alcohol and dilute alkalis, reppd. by acids (Virey, *J. Ph.* 1844, 151).

CARAMEL. A black substance obtained by heating cane-sugar at c. 200°. It is said to be a mixture of caramelan $C_{12}H_{18}O_9$, caramelen $C_{36}H_{50}O_{25}$, and caramelin $C_{96}H_{102}O_{51}$. They all reduce Fehling's solution. Dilute (84 p.c.) alcohol extracts caramelan, cold water then dissolves caramelen, leaving caramelin. Caramelan is a colourless, brittle, deliquescent resin.—$C_{12}BaH_{16}O_9BaO$.—$C_{12}PbH_{16}O_9$.—$C_{12}PbH_{16}O_9PbO$. Caramelen is a mahogany-coloured solid.—$C_{36}H_{48}BaO_{25}$.—$C_{36}H_{48}PbO_{25}$. Caramelin is a glittering black solid, sol. boiling water.—$C_{96}H_{100}BaO_{51}$.—$C_{96}H_{100}BaO_{51}BaO$.—$C_{96}H_{100}PbO_{51}$ (Gélis, *A. Ch.* [3] 52, 352). Caramelan and caramelen are crystalloids, caramelin is a colloid. The formulæ and purity of these bodies are, of course, very doubtful; other

observers have arrived at somewhat different results, indeed the nature of the resulting products depends upon the temperature used in preparing them (Péligot, *A. Ch.* [2] 67, 172; Völckel, *A.* 85, 59; Maumené, *C. R.* 39, 422; Graham, *C. J.* 15, 258; Thomson a. Sherlock, *C. N.* 25, 242, 282).

CARAWAY OIL. Oil of caraway contains a terpene (*q. v.*) $C_{10}H_{16}$ identical with citrene, and carvol (*q. v.*) $C_{10}H_{14}O$.

CARB-ACETO-ACETIC ETHER is *mesitene-lactone carboxylic acid*, p. 20.

CARBACETOXYLIC ACID $C_5H_4O_4$. A syrupy acid, said to be formed by the action of moist Ag_2O on β-chloro-propionic acid and on $\alpha\alpha$-di-chloro-propionic ether. Reduced by sodium-amalgam to glyceric acid, and by HI to pyruvic acid (Wichelhaus, *A.* 143, 7; 144, 351; Klimenko, *B.* 3, 468; 5, 477; 7, 1406; *cf.* Beckurts a. Otto, *B.* 10, 2039).

TRI-CARBALLYLIC ACID $C_6H_8O_6$ *i.e.* $CO_2H.CH(CH_2.CO_2H)_2$. *s-Propane tri-carboxylic acid.* Mol. w. 176. [158°]. S. 40·5 at 14°.

Formation.—1. In the preparation of sugar from beet-root (Lippmann, *B.* 11, 707; 12, 1649; Weyer, *C. J.* 38, 864).—2. By the saponification of its nitrile which is prepared by the action of KCy on *s*-tri-bromo-propane in alcohol (M. Simpson, *Pr.* 12, 236; 14, 77; *C. J.* 18, 331).—3. By reducing aconitic acid or its ether with sodium-amalgam (Dessaignes, *C. R.* 55, 510; Wichelhaus, *A.* 132, 61; Hlasiwetz, *Z.* 1864, 734).—4. By the action of potash on the product of the action of KCy on β-chloro-isocrotonic ether (obtained from aceto-acetic ether and PCl_5) (Claus a. Lischke, *B.* 14, 1089).—5. In the same way from α-chloro-crotonic ether or from di-chloro-propylene (*i.e.* dichlorhydrin) (Claus, *B.* 5, 358; 9, 223; *A.* 170, 131; 191, 63).—6. Appears to be formed by the action of HCl and $KClO_3$ on gallic acid (Schreder, *A.* 177, 292).—7. Acetyl-succinic ether is converted by Na into acetyl-tri-carballylic ether $CH_3CO.C(CH_2.CO_2Et)_2.CO_2Et$ whence alcoholic KOH or baryta-water produce tri-carballylic acid (Miehle, *A.* 190, 322).—8. By the oxidation of di-allyl-acetic acid by dilute HNO_3 (Wolff, *A.* 201, 53).—9. By boiling citraconic acid with zinc and HCl (Behrmann a. Hofmann, *B.* 17, 2692).—10. From propane tetra-carboxylic acid $(CO_2H.CH_2)_2C(CO_2H)_2$ by heat (Bischoff, *A.* 214, 66).

Properties.—Hard short trimetric prisms (from water); v. sol. water and alcohol, sl. sol. ether. The ammonium salt gives with $BaCl_2$ or $CaCl_2$ no pp., even on adding NH_3. $Pb(OAc)_2$ gives a white pp. Fe_2Cl_6 gives a red pp.

Salts. — Na_2HA''' 2aq(?) — KH_2A'''. — $Ca_3A'''_2$ 4aq.—$BaHA'''$.—$Ba_3A'''_2$ 6aq.—$Pb_3A'''_2$—$Cu_3A'''_2$.—Ag_3A'''.

Tri-ethyl ether Et_3A''' (c. 300°).

Tri-isoamyl ether $(C_5H_{11})_3A'''$ (above 360°).

CARBAMIC ACID CH_3NO_2 *i.e.* $NH_2.CO_2H$. *Amido-formic acid. Amide of carbonic acid.* Not known in the free state. The **ammonium salt** is formed by the union of dry or moist CO_2 (1 vol.) with gaseous NH_3 (2 vols.) (J. Davy, *N. Ed. P. J.* 16, 345; Rose, *P.* 46, 352; *A.* 30, 47). Formed also by sublimation of neutral ammonium carbonate, and therefore occurs in commercial ammonium carbonate. Formed also by oxidising glycocoll, leucine, tyrosine, and albumen, with alkaline $KMnO_4$ (Drechsel, *J. pr.* [2] 12, 417; *cf.* Hofmeister, *J. pr.* [2] 14, 173). It may be conveniently prepared by digesting commercial ammonium carbonate with saturated aqueous NH_3 for 30 or 40 hours at 20°-25° (Divers, *C. J.* 23, 215; *cf.* Kolbe a. Basaroff, *C. J.* 21, 194).

Reactions.—1. *Acids* decompose carbamates with formation of CO_2 and NH_3.—2. *Boiling water* converts carbamates into carbonates.—3. *Strongly heating* converts the Na salt into sodium cyanate and H_2O (Drechsel, *J. pr.* [2] 16, 199).

Salts.—The carbamates are soluble in water (difference from most carbonates).—NH_4A' (*v. supra*). Deliquescent plates. Its aqueous solution quickly changes to carbonate, but it is stable in presence of excess of NH_3 in the cold. At 60° it is completely split up into CO_2 and NH_3 (Naumann, *A.* 160, 1; *B.* 18, 1157; Horstmann, *A.* 187, 48; Erckmann, *B.* 18, 1154). In a sealed tube at 140° it forms urea.—$NaA'x$aq: formed by adding NaOEt to an alcoholic solution of the ammonium salt; prisms.—KA': deliquescent.—CaA'_2 aq: ppd. by adding lime and alcohol to a solution of NH_4A' at 0°; crystalline powder, sol. water, the solution quickly deposits $CaCO_3$. When strongly heated it leaves calcium cyanamide.—SrA'_2.—BaA'_2.

Chloride $OC(NH_2)Cl$. [c. 50°]. (62°). Prepared by passing a stream of dry $COCl_2$ into NH_4Cl heated to about 400°. Long broad needles. Strong odour. On keeping it slowly changes into cyamelide with evolution of HCl. By water it is decomposed into NH_4Cl and CO_2. On vaporisation it probably dissociates into cyanic acid and HCl, which again recombine on cooling. By CaO it is converted into cyanic acid. With aromatic hydrocarbons in presence of Al_2Cl_6 it gives amides of aromatic acids (Gattermann a. Schmidt, *B.* 20, 858).

Carbamic ethers. *Urethanes.*

Preparation.—1. From chloro-formic ethers and NH_3.—2. From cyanic acid and alcohols.—3. From cyanogen chloride and alcohols.—4. By heating alcohols with urea nitrate.

Properties.—Solid substances, sl. sol. water, v. sol. alcohol and ether; may be distilled.

Reactions.—1. Heating with NH_3 gives urea. 2. P_2O_5 gives cyanates.—3. Alcoholic KOH acts upon carbamic ethers of the fatty series according to the equation: $NH_2.CO_2C_nH_{2n+1} + KOH = KNCO + C_nH_{2n+1}OH + H_2O$ (Arth, *Bl.* [2] 45, 702; *A. Ch.* [6] 8, 428). Bornyl and menthyl carbamates act similarly.

Methyl ether MeA'. [52°]. (177°). S. 217 at 11°; S. (alcohol) 73 at 15° (Echevarria, *A.* 79, 110).

Ethyl ether EtA'. *Urethane.* Mol. w. 89. [c. 50°]. (c. 182°). Formed by the above methods (Dumas, *A. Ch.* [2] 54, 233; *A.* 10, 284; Liebig a. Wöhler, *A.* 54, 370; 58, 260; Wurtz, *A.* 79, 286; *C. R.* 22, 503; Bunte, *Z.* [2] 6, 96; *A.* 151, 181). Also from carbonic ether and NH_3 (Cahours, *C. R.* 21, 629; *A.* 56, 266).

Reactions.—Alcoholic potash, at the ordinary temperature, gives large crystals of potassium cyanate. In this case $NH_2.CO_2K$ is not formed as an intermediate product. A solution of

urethane in absolute ether, treated with K or Na gives the derivatives $KNH.CO_2Et$, and $NaNH.CO_2Et$. Of these, the Na derivative is sufficiently stable for analysis. It is v. sol. absolute alcohol, insol. absolute ether. With alcoholic potash containing water K_2O_2 is obtained. The body $HgN.CO.OEt$ is obtained by mixing alcoholic solutions of urethane, $HgCl_2$, and KHO (Mulder, *R. T. C.* 6, 170).

Acetyl derivative $NHAc.CO_2Et$. [78°] (Conrad a. Salomon, *J. pr.* [2] 10, 28).

Chloro-ethyl ether $H_2N.CO_2.C_2H_4Cl$. [76°]. From NH_3 and the chloro-ethyl ether of chloroformic acid. Prisms. V. sol. water, alcohol and ether (Nemirowsky, *J. pr.* [2] 31, 174).

n-Propyl ether PrA'. [53°]. (195°) (Cahours, *J.* 1873, 748; Roemer, *B.* 6, 1102). Long prisms.

Isobutyl ether C_4H_9A'. [55°]. (207°) (Mylius, *B.* 5, 973; Humann, *A. Ch.* [3] 44, 340; *A.* 95, 372).

Isoamyl ether $C_5H_{11}A'$. [60°]. (220°) (Medlock, *A.* 71, 106; Wurtz, *J. Ph.* [3] 20, 22). Needles.

Octyl ether $C_8H_{17}A'$. [55°]. (135°) at 25 mm.; (231°) at 760 mm. On distillation it is partially converted into cyanuric acid (Arth, *C. R.* 102, 977).

Bornyl carbamate v. p. 523.

Menthyl carbamate v. MENTHOL.

CARBAMIDE v. UREA.

CARBAMIDO- v. URAMIDO-.

CARBAMINES. *Carbylamines. Iso-nitriles.* Compounds of the formula R.N:C.

Formation.—1. By distilling primary monamines with chloroform and alcoholic potash: $RNH_2 + CHCl_3 + 3KOH = 3KCl + RNC + 3H_2O$ (Hofmann, *A.* 144, 114; 146, 107).—2. By treating an alkyl iodide (1 mol.) with silver cyanide (2 mols.) a double salt RNCAgCy is formed; on distilling this compound with conc. aqueous KCy there is formed KCyAgCy and the carbamine passes over (Gautier, *A.* 146, 119; 149, 29, 155; 151, 239). $HgCy_2$ and $ZnCy_2$ may also be used in preparing carbamines (Calmels, *Bl.* [2] 43, 82).—3. In small quantity in preparing nitriles by distilling potassium alkyl sulphates with potassium cyanide.—4. By distilling the compounds of thio-carbimides with tri-ethyl-phosphine (Hofmann, *B.* 3, 766; *Z.* 7, 29).

Properties.—Volatile stinking poisonous oils.

Reactions.—1. *Alkalis* have no action.—2. *Mineral acids* instantly convert them into alkylamines and formic acid: $RNC + 2H_2O = RNH_2 + H.CO_2H$. *Water* at 180° acts similarly. 3. Dry HCl forms a compound, quickly decomposed by water as in 2.—4. *Organic acids* form alkyl-formamides.—5. EtI forms a compound (difference from nitriles).—6. HgO oxidises them to alkyl cyanates R.N:CO, alkyl-formamides being also formed (Gautier, *A.* 149, 311).

CARBAMINE-CYANIDE or **CARBAMINE-CYANAMIDE** so called is described as AMIDO-DI-CYANIC ACID. Its derivatives are described as ETHYL-CARBIMIDO-UREA, CARBIMIDO-ETHYL-UREA, &c.

CARBANIL v. PHENYL CYANATE.

CARBANILIC ACID v. PHENYL-CARBAMIC ACID.

CARBANILIDE v. s-DI-PHENYL-UREA.

CARBANILIDO- v. PHENYL-URAMIDO-.

CARBAZOLE $C_{12}H_9N$ *i.e.* $<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>NH$. Mol. w. 167. [238°]. (352° cor.). V.D. 5·86 (calc. 5·85). S. (alcohol ·92 at 14°; 3·88 at 78°. S. (toluene) ·55 at 16·5; 5·46 at 100° (Bechi, *B.* 12, 1978).

Occurrence.—Among the products of the distillation of coal tar; hence it occurs in crude anthracene (Graebe a. Glaser, *B.* 5, 12, 376; *A.* 163, 343; 167, 125; 174, 180; 202, 21; Zeidler, *A.* 191, 297).

Formation.—1. By passing vapour of aniline or diphenylamine through a red-hot tube.—2. From imido-di-phenyl sulphide (thio-di-phenyl-amine) by boiling $HN<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>S$ with freshly reduced copper for 2 or 3 hours; the yield is about 60 p.c. (Goske, *B.* 20, 233).

Properties.—White laminæ or tables. Easily sublimes. A solution in conc. H_2SO_4 is turned green by HNO_3. May be distilled over red-hot zinc-dust without change. Although an imide, it forms a compound with picric acid and its acetyl derivative is obtained with difficulty.

Reactions. — 1. It is not affected by conc. HClAq or alcoholic KOH even at 300°. Cold conc. H_2SO_4 dissolves it without change, but at 100° a di-sulphonic acid results. — 2. HNO_3 forms nitro- compounds.—3. *Sodium-amalgam* does not reduce it in alcoholic solution, but HI and P at 210° reduce it to carbazoline $C_{12}H_{15}N$.—4. By exhaustive chlorination with $SbCl_5$ it yields per-chloro-diphenyl or per-chloro-benzene according to circumstances as yet undetermined (Merz a. Weith, *B.* 16, 2875).—5. By heating with *oxalic acid* the compound $C_{37}H_{25}N_3O$ or $HO.C(C_6H_3<\begin{matrix}NH\\C_6H_4\end{matrix}>)_3$ is obtained. It forms minute crystals which very readily yield blue solutions (carbazole blue) on oxidation (Suida, *B.* 12, 1403; Bamberger a. Müller, *B.* 20, 1903).

Potassium derivative $C_{12}H_8NK$. From carbazole and KOH at 230°. Picric acid compound $C_{12}H_9N\,C_6H_2(NO_2)_3OH$. [182°]. From carbazole (1 pt.) and picric acid ($1\frac{1}{3}$ pts.) in toluene. Red prisms; v. sl. sol. cold benzene or alcohol. Decomposed by a large quantity of alcohol, by water, and by alkalis.

Nitrosamine $C_{12}H_8N.NO$. [82°]. Nitrous acid in an alcoholic solution of carbazole forms mono- and di-nitro-carbazole. If carbazole (3 g.) be mixed with acetic acid (60 g. of S.G. 1·04) and ether (60 g.) be poured in, on adding KNO_2 the nitrosamine is dissolved in the ether as fast as it is formed, and crystallises out on evaporation. Long flat golden needles. Soluble in ether, CS_2, chloroform, glacial acetic acid and benzene. It is decomposed if heated with alcohol mixed with an acid, carbazole being regenerated. Alcoholic KOH turns it blood-red. Reducing agents regenerate carbazole. Conc. H_2SO_4 gives a dark-green colour (Zeidler, *A.* 191, 305).

Acetyl derivative $C_{12}H_8NAc$. [69°]. (above 360°). From carbazole and Ac_2O at 250°. Slender needles (from water); v. sl. sol. water, v. e. sol. alcohol. Erdmann's solution does not turn it green. Its picric acid compound is orange.

References. — Bromo-, Chloro-, Nitro-, Methyl-, and Ethyl-, carbazole.

CARBAZOLE TETRAHYDRIDE $C_{12}H_{13}N$. [120°]. (c. 328°). Formed, together with hydrogen, by heating carbazoline hydrochloride at 300°. Crystallises from alcohol. V. e. sol. alcohol, insol. water. Does not combine with acids. Reduced by HI and P to carbazoline. The picric acid compound $C_{12}H_{13}NC_6H_2(NO_2)_3OH$ forms brown laminæ.

CARBAZOLE *v*-CARBOXYLIC ACID $C_{13}H_9NO_2$ *i.e.* $C_{12}H_8N.CO_2H$. [272°]. From potassium carbazole and CO_2 at 270°. Micaceous scales or flattened prisms with faint blue fluorescence: insol. water, sl. sol. cold alcohol (Ciamician a. Silber, *G.* 12, 272).

CARBAZOLINE $C_{12}H_{15}N$. *Carbazole hexahydride.* [99°]. (297° i. V.). V.D. 6·13 (5·99 calc.). Formed by heating carbazole (3 pts.) with (12 pts. of) HIAq (127°) and amorphous P (1 pt.) at 220°. White needles (from alcohol); may be sublimed; volatile with steam; v. e. sol. alcohol and ether, v. sl. sol. water. HI and P at 330° reduce it to *diphenyl decahydride* $C_{12}H_{20}$. Does not combine with picric acid.

Salts.—B'HCl: v. e. sol. water.—B'HBr: tables.—B'HI.

Acetyl derivative $C_{12}H_{14}NAc$. [98°]. From carbazoline and Ac_2O at 110°. Needles (from alcohol).

CARBIDES. *Compounds of carbon with one other more positive element.* A carbide of iron Fe_3C probably exists in cold rolled steel; other carbides of this metal are described, but their existence is doubtful. Silver is said to form three carbides, Ag_4C, Ag_2C, and AgC. Nickel takes up a small quantity of carbon when strongly heated with charcoal, but no definite compound has yet been prepared. We have very little definite information regarding this class of compounds (*v.* Iridium, Iron, Nickel, Palladium, Platinum, and Silver). M. M. P. M.

CARBIMIDE *v.* Cyanic acid.

CARBIMIDO-ALLYL-THIO-UREA $C_5H_7N_3S$ *i.e.* $SC<^{NC_3H_5}_{NH}>C:NH$ or $C_3H_5NH.CS.N:C:NH$. *Allyl-thio-carbamine-cyamide.* Formed, as the crystalline sodium salt, by mixing allyl-thio-carbimide and sodium cyanamide. Decomposed by acids into its constituents (Wunderlich, *B.* 19, 448).

CARBIMID-AMIDO-BENZOIC ACID is Guanido-di-benzoic acid *v.* p. 157.

CARBIMIDAMIDO-BENZOYL *v.* Oxy-quinazoline and p. 155.

CARBIMIDO-CYANAMIDE *v.* Amido-dicyanic acid, p. 163.

CARBIMIDO-ETHYL-THIO-UREA $C_4H_7N_3S$ *i.e.* $SC<^{NEt}_{NH}>C:NH$ or $EtHN.CS.N:C:NH$. *Ethyl-thio-carbamine-cyamide.* Formed, as the crystalline sodium salt, by mixing ethyl-thio-carbimide and sodium cyanamide. Decomposed by acids into its constituents (Wunderlich, *B.* 19, 448).

CARBIMIDO-ETHYL-UREA $C_4H_7N_3O$ *i.e.* $OC<^{NEt}_{NH}>C:NH$ or $EtHN.CO.N:C:NH$. *Ethyl-carbamine-cyamide.* Formed, as the crystalline sodium salt, by mixing ethyl cyanate and sodium cyanamide. Decomposed into its constituents by acids. Forms a green crystalline copper compound (Wunderlich, *B.* 19, 448).

CARBIMIDO-METHYL-THIO-UREA $C_3H_5N_3S$ *i.e.* $SC<^{NMe}_{NH}>C:NH$ or $MeHN.CS.N:C:NH$. *Methyl-thio-carbamine-cyamide.* Formed, as the crystalline sodium salt, by mixing methyl-thiocarbimide and sodium cyanamide. Decomposed by acids into its constituents (Wunderlich, *B.* 19, 448).

CARBIMIDO-PHENYL-THIO-UREA $C_8H_7N_3S$ *i.e.* $SC<^{NPh}_{NH}>C:NH$ or $PhNH.CS.N:C:NH$. *Phenyl-thio-carbamine-cyamide.* Formed, as the crystalline sodium salt, by mixing phenyl-thiocarbimide and sodium cyanamide. Decomposed by acids into its constituents (Wunderlich, *B.* 19, 448).

DI-CARBIN-TETRA-CARBOXYLIC ACID *v.* Ethylene-tetra-carboxylic acid.

CARBINOL. A name given by Kolbe to methyl alcohol, but used only in describing alcohols derived therefrom by displacement of hydrogen of its methyl by one or more alkyls. *Cf.* Alcohols.

CARBINYL. The corresponding term for the alcohol radicles of the alkyl-carbinols; thus, Me_3C may be called tri-methyl-carbinyl.

CARBO-ACETO-ACETIC ETHER *v.* p. 20.

CARBO-ALLYL-PHENYL-AMIDE *v.* Phenyl-allyl-cyanamide.

CARBO-DI-BUTYL-DI-PHENYL-IMIDE *v.* Di-butyl-di-phenyl-cyanamide.

CARBO-ISO-BUTYRALDINE $C_9H_8N_2S_2$ *i.e.* $(NH_2)CS.S.N(C_4H_8)_2$. [91°]. From iso-butyraldehyde, CS_2, and aqueous NH_3. Prisms, insol. water, sol. alcohol (Pfeiffer, *B.* 5, 701).

CARBO-CAPRO-LACTONIC ACID *v.* *Lactone of* Oxy-propyl-succinic acid.

Di-carbo-capro-lactonic acid *v.* *Lactone of* Oxy-penta-ne-tetra-carboxylic acid.

CARBOCINCHOMERONIC ACID is Pyridine tri-carboxylic acid.

CARBO-GLUCONIC ACID $C_7H_{14}O_8$. An amorphous acid whose NH_4 salt is obtained by treating glucose or cane-sugar with aqueous HCN (Schützenberger, *Bl.* [2] 36, 144).

CARBO-DI-GLYCOLLIC ETHER *v.* Glycollic acid.

CARBOHOMOPYRROLIC ACID *v.* Methyl-pyrrol-carboxylic acid.

CARBOHYDRATES. A term applied to compounds which may be represented by the formula $C_x(H_2O)_y$ where x is 6, 6, or 12, and y is 5, 6 or 11, and to compounds derived from several such molecules by abstraction of water. They are non-volatile solids, and the non-saccharine members of the group may be converted by boiling dilute acids into a sugar, usually glucose (dextrose). They contain hydroxyl. On oxidation they frequently give rise to oxalic, racemic, saccharic, and mucic acids. Most of them are optically active. Cellulose is insoluble in water; the gums dissolve, or at least swell up, in water, but are ppd. by alcohol. Sugars are soluble in water, are not reppd. by alcohol, and have a sweet taste. Iodine turns starch blue, and affects cellulose in the same way after it has been treated with a dehydrating agent. The carbohydrates vary also in their behaviour towards alkaline copper solutions, and as regards

fermentation by yeast. They are described in the articles ARABIC ACID, CELLULOSE, DEXTRIN, STARCH, SUGAR, ETC.

CARBOLIC ACID *v.* PHENOL.

CARBO-MESYL *v.* METHYL-OXINDOLE.

CARBO-DI-NAPHTHYL-IMIDE *v.* DI-NAPHTHYL-CYANAMIDE.

CARBON GROUP OF ELEMENTS.—*Carbon* and *Silicon*. Of these elements, carbon occurs in the free state in the forms of diamond, graphite, and amorphous carbon; silicon is not known as such in nature, but combined with oxygen it is one of the most widely-distributed elements. Diamond was regarded by Newton as a combustible body because of its great refractive power: in 1694 the Florentine academicians succeeded in burning small pieces of diamond; and in the early years of this century Davy proved it to be pure carbon. In early times graphite was thought to be very similar to lead; hence the name *plumbago*; for a time it was confused with molybdenum-glance, but in 1799 Scheele proved it to be closely related to coal in its composition. It is only in somewhat recent times that approximately pure graphite has been obtained. Charcoal is the commonest form of impure amorphous carbon; this modification of carbon can be obtained approximately pure only with considerable difficulty.

After the earths had been proved to be metallic oxides in 1807, it was generally supposed that the common earth-like body silica would also be found to contain oxygen and a metal. In 1823 Berzelius decomposed silica and obtained the non-metal silicon, in the form of a brown amorphous powder. A good many years later Deville prepared crystallised silicon in two forms, one more or less resembling diamond, and the other, graphite. The leading properties of the two elements are as follows:—

	CARBON.	SILICON.
Atomic weights	11·97	28

Many compounds of each element have been gasified. Molecular weights unknown: (?) probably greater than C_2 and Si_2.

Melting-points	Does not melt at any temperature hitherto attained.	1,100°–1,300° (uncertain).
Specific gravities (approximate)	Diamond 3·5; graphite 2·25; amorphous 1·5–1·9.	Graphitoidal 2·2–2·5 (doubtful).
Specific heats	0·46 (at about 1000°).	0·203 (at about 250°)

The specific heat of either element increases rapidly as temperature increases from −50°: the rate of this increase is, however, very small after about 500° for carbon and about 150° for silicon. The specific heats of diamond and graphite vary considerably at temperatures below about 600°, but from this point upwards the values are practically identical.

Atomic weight / *Spec. grav.* (approximate)	4·5	11·2

Heats of formation of various compounds (Thomsen, Berthelot, &c.).
(Generally from amorphous Carbon or Silicon.)

$[M,H^4]$	21,750	24,800
$[M,Cl^4]$	21,000	157,600 (product liquid)
$[M,O^2]$	96,960	219,200
$[M,S^2]$	−26,000	40,000
Change of amorphous M to crystalline M	3,000	8,100

Heats of neutralisation of aqueous solutions of CO_2 and SiO_2 (Thomsen).

n	$[CO^2Aq, nNaOHAq]$		n	$[SiO^2Aq, n NaOHAq]$
1	11,000	diff. = 9,150	$\frac{1}{2}$	3,240
2	20,150		1	4,315
			$\frac{4}{3}$	4,730
			2	5,230
			4	5,410

Silicic acid shows no constant neutralisation-point. The quantity of heat produced is a hyperbolic function of the quantity of soda added, and approaches a probable maximum of 6,300 gram-units for one formula-weight of SiO_2 (*v.* SILICATES).

Physical properties	*Diamond*: hardest known substance; crystallises in regular forms, octahedral predominating; bad conductor of electricity; refractive index large ($\mu_D = 2·430$); lustre very marked; usually colourless and transparent, but sometimes green, brown, or yellow,	*Adamantine*: very hard, scratches glass; dark iron-grey colour, reddish by reflected light; crystallises in forms derived from a rhombic octahedron. *Graphitoidal*: softer than adamantine but scratches glass; may be pulverised; metal-like lustre, leaden-

TABLE—*cont.*

	CARBON.	SILICON.
	Graphite: crystallises in hexagonal forms; good conductor of electricity; tough and difficult to pulverise; grey, metal-like appearance. *Amorphous*: black powder; very porous, absorbs large quantities of gases and of many colouring matters from solutions.	grey colour; crystallises in leaflets composed of octahedra; good conductor of electricity. *Amorphous*: brown powder; heated out of contact with air to high temperature it contracts and becomes crystalline; bad conductor of electricity; dissolves in molten Al or Zn and crystallises out on cooling.
Occurrence and preparation	The three forms occur in nature, but neither graphite nor amorphous pure; constituent element of all animal and vegetable matter; carbonates very widely distributed; graphite prepared by dissolving amorphous in molten iron, or by decomposing by heat the CN compounds in the mother liquor of soda manufacture, &c.: approximately pure amorphous, prepared by washing sugar-charcoal in acid, alkali, and water, and strongly heating in chlorine; or by decomposing CO_2 by Na, &c.	Very widely distributed as silicates of Ca, Mg, Fe, Al, &c.; amorphous obtained by action of K on hot $SiCl_4$, SiF_4, or K_2SiF_6; graphitoidal obtained by melting Al with K_2SiO_3 and cryolite, or by decomposing $SiCl_4$ at a high temperature by Na; adamantine obtained by melting Zn with K_2SiF_6 and Na.
Chemical properties.	Allotropy marked. Diamond heated by powerful battery in absence of oxygen gets grey-black and coke-like but does not volatilise; heated in air combustion begins at 950°–1000°. Graphite not affected at any temperature in absence of oxygen; oxidised by repeated treatment with $KClO_3$ and HNO_3 to *graphitic acid* $C_{11}H_4O_5$ (or O_6), a yellow solid, sl. sol. water, acting towards alkaline bases like a feeble acid. Amorphous burns easily in air; combines with H at a very high temperature to form C_2H_2; also combines directly with S to form CS_2, with O to form CO and CO_2, and under special conditions with N to form C_2N_2; compounds with halogens formed indirectly; combines directly with Ir, Fe, Ni, Pd, Pt, Ag, and perhaps some other metals. Carbon a negative element; does not form salts by replacing H of acids; CO_2 an anhydride; an aqueous solution of CO_2 probably contains the dibasic acid H_2CO_3, salts of this acid well marked; H_2CS_3 prepared. Atom of C is tetravalent; C atoms tend to combine with each other; vast number of compounds produced by addition of other atoms to groups of C atoms.	Allotropy marked. Amorphous Si burns easily in air to SiO_2; graphitoidal does not oxidise when heated; adamantine not even at a white heat in oxygen; adamantine Si oxidised at red heat in CO_2 (giving $CO + SiO_2$), also by strongly heating with K_2CO_3 or Na_2CO_3 (giving $CO + SiO_2 + C$), but not changed by molten $KHSO_4$, or by heating with KNO_3 if temp. at which that salt decomposes is not reached. Amorphous Si soluble in HFAq giving H_2SiF_6Aq and hydrogen, also in strong hot potash ley giving K_2SiO_3Aq and hydrogen; adamantine Si insoluble in HFAq and hot alkali solutions. Si does not directly combine with H, SiH_4 produced by action of HClAq on compound of Si and Mg; combines with S at high temperature to form SiS_2; with O to form SiO_2; with Cl, Br, or I, to form $SiCl_4$, $SiBr_4$, or SiI_4; and with N at white heat to form Si_2N_3; combines directly with Al, Cu, Fe, Mg, Mn, Ni, Pt, and perhaps some other metals. SiO_2 an anhydride; probable existence of several silicic acids; $SiO(OH)_2$ probably present in solution obtained by neutralising K_2SiO_3Aq by HClAq and dialysing; this solution very readily gelatinises. Atom of Si is tetravalent, and, to some extent at least, atoms of Si tend to combine together and form groups which combine with other atoms, forming molecules similar to those of the *organic* compounds.

General formulæ and characters of compounds.

MO, MO_2, MS_2, (SiO unknown, ? CS and C_2S_3); MO_3H_2 (neither known except (?) in aqueous solution, *v.* CARBON and SILICON), CS_3H_2; MH_4; C_nH_{2n+1}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-6}, &c., &c., and a vast number of derivatives; MX_4 ($X = Cl$, Br, I, or in case of Si also $= F$), M_2X_6 ($X = Cl$, Br, or I where $M = Si$, $X = Cl$ or Br where $M = C$), C_2Cl_4, C_2Br_4, &c.; SiF_6H_2; CH_3Cl, CH_2Cl_2, $CHCl_3$, $SiHCl_3$, $SiHI_3$, &c.; C_2N_2, CNH and salts, $C_6N_6FeH_4$ and salts, $C_6N_6FeH_3$ and salts, $C_5N_5NOFeH_2$ and salts, &c., &c.; Si_2N_3 &c. The compounds of C and Si exhibit considerable differences in their properties; CO and CO_2 are gases, SiO_2 is a very fixed solid; CS_2 is a liquid, SiS_2 a solid; CCl_4 is not acted on by water, $SiCl_4$ is at once decomposed into SiO_2 and HCl; Si readily forms a fluoride and also a double fluoride with hydrogen, no corresponding compounds of C are known; CH_4 is a stable gas, SiH_4 is oxidised by mere contact with air and is easily decomposed by heat (at 400°); Si (amorphous) dissolves in potash evolving hydrogen and forming a silicate, carbon is unacted on by alkalis. Both elements form many compounds with H and O (alcohols, ethers, acids &c.), the composition of which is similar, in some cases the properties of the Si compounds closely resemble those of C, *e.g.* $C(C_2H_5)_3H$ and $Si(C_2H_5)_3H$, $C(C_2H_5)_3OH$ and $Si(C_2H_5)_3OH$; but in other cases the properties of the two classes of compounds differ much, *e.g.* $CH_3.CO_2H$ and $C_2H_5.CO_2H$ are liquids soluble in water, but $CH_3.SiO_2H$ and $C_2H_5.SiO_2H$ are amorphous solids insoluble in water. Many silicates and carbonates are isomorphous. Silicates, except those of the alkali metals, are insoluble in water, and most of them are with difficulty decomposed by acids; the normal carbonates of the alkali metals are soluble in water, other normal carbonates are insoluble; aqueous solutions of acid carbonates are generally easily decomposed by heat yielding either normal or basic carbonates; the normal carbonates of the alkali metals are not decomposed by heat alone, other normal carbonates are decomposed into metallic oxide and CO_2.

Group IV. of the elements, as the elements are classified by the application of the periodic law, contains the following:—

	Series					
Even	2	4	6	8	10	12
	C	Ti	Zr	Ce	–	Th
Odd	3	5	7	9	11	
	Si	Ge	Sn	–	Pb	

The metals titanium, zirconium, and germanium show considerable analogies with tin; cerium and thorium are usually classed together among the rarer earth-metals, and lead is generally considered apart from other metals: nevertheless there are well-marked analogies between all the elements which comprise Group IV. of the periodic system. Titanium is an amorphous body closely resembling amorphous silicon; it forms the compounds TiF_4, $TiCl_4$, $TiBr_4$, TiI_4, Ti_2Cl_6, TiO_2 (probably $TiO(OH)$ and $Ti(OH)_4$), Ti_2O_3, Ti_3N_4, &c.; titanates are known (M_2TiO_3), many of them isomorphous with silicates and carbonates. Ti is more metallic than C or Si, it forms a sulphate $Ti(SO_4)_2$, and other salts wherein the hydrogen of acids is replaced by titanium. Zirconium again is more decidedly metallic than titanium; it forms a series of well-marked salts $Zr(SO_4)_2$, $Zr4NO_3$, &c., &c. On the other hand Zr resembles C and Si in that it has been obtained both as an amorphous powder, and also in crystals which resemble Si in their behaviour towards acids; zirconates (M_2ZrO_3) are also known. Germanium forms oxides, chlorides, and sulphides, &c. (GeX and GeX_2, $X = O = S = Cl_2$), resembling those of Sn; it is, however, more markedly non-metallic in its chemical functions than Sn; physically Ge is decidedly metallic. Cerium forms two oxides Ce_2O_3 and CeO_2; the former dissolves in acids forming a series of salts of which Ce_23SO_4 is a type; CeO_2 is a peroxide, it dissolves in HCl with evolution of Cl and formation of $CeCl_3$, but a sulphate $Ce(SO_4)_2$ is known corresponding to the sulphates of Ti and Zr. Ce also forms a fluoride CeF_4, a double fluoride $3KF.2CeF_4$, and a chloride Ce_2Cl_6. Thorium again approaches more closely than cerium to Zr and Ti; it is a dark-coloured amorphous powder resembling Si, but more soluble in acids than Si, Zr, or Ti; it forms the compounds $ThCl_4$, ThF_4, K_2ThF_6, ThO_2, &c.; the sulphate is $Th(SO_4)_2$, and other analogous salts are known. Tin forms the two oxides and chlorides SnO and SnO_2, $SnCl_2$ and $SnCl_4$; the hydrates of SnO_2 are feeble acids, producing stannates (M_2SnO_3) and metastannates ($M_2Sn_5O_{11}$), both of which are easily decomposed by dilute acids or by heat. Both the stannous salts *e.g.* $SnSO_4$, and the stannic salts *e.g.* $Sn(SO_4)_2$, are well-marked compounds. Lead is decidedly metallic in its character; it forms four oxides PbO, Pb_3O_4, Pb_2O_3, and PbO_2; the last is a peroxide, and it may also be regarded as an anhydride inasmuch as plumbates (M_2PbO_3) exist, but these salts are very unstable and easily decomposed. The best-marked salts of lead are derived from the oxide PbO, *e.g.* $PbCl_2$, $Pb2NO_3$, $PbSO_4$, &c.; $PbCl_4$ has not been obtained pure, but this series of salts is represented by the tetramethide $Pb(CH_3)_4$ which is stable as a gas. The atoms of all the elements of Group IV., so far as evidence has been obtained, are tetravalent. Looking at the properties of these elements as a whole, it may be said that carbon is to a considerable extent set apart from the others, but that it is more closely allied to silicon than to any other member of the group; that titanium and zirconium are closely related; and that tin and lead, while showing distinct analogies with the rest of the group, are yet each characterised by properties which mark them off from the other elements. Not much can yet be said regarding cerium and thorium; they require further study.

For more details and descriptions of the various elements see the articles on these elements; also *v.* TITANIUM GROUP OF ELEMENTS; also *v.* CARBONATES, NITRATES, SULPHATES, &c. In some of their physical properties carbon and silicon, especially the latter, resemble boron, but boron must be classed with those elements the atoms of which are trivalent: *v.* BORON.

M. M. P. M.

CARBON C. At. w. 11·97. Mol. w. unknown; element has not been gasified. S.G. diamond

18° 3·514 (Schrötter, *Sitz. W.* 63, (2nd pt.) 462), 3·518 (Baumhauer, *Ar. N.* 8, 1). S.G. graphite 2·11 to 2·26 (Kenngott, Brodie, Mène; *Sitz. W.* 13, 469; *A.* 114, 7; *C. R.* 64, 104). S.G. amorphous charcoal 1·45 to 1·7 (*v.* Violette, *A. Ch.* [3] 39, 291). S.G. hard gas-coke 2·356 (Marchand a. Meyer). S.H. about ·5 at 1000° (*v. infra*). C.E. (diamond, linear at 40°) ·00000118; (diamond, cub. at 40°) ·00000354; (graphite, linear at 40°) ·00000786; (Fizeau, *C. R.* 62, 1133; 68, 1125). $\mu_D=2·46$, $\mu_E=2·479$, for diamond (Schrauf, *P.* 112, 588). E.C. graphite, ·082 (Hg at 0° = 1) [varies much for different specimens] (Muraoka, *W.* 13, 307). E.C. hard gas-coke, ·01 (Hg at 0° = 1) (Muraoka, *l.c.*). Crystalline form; diamond, regular octahedra and forms derived therefrom; graphite, hexagonal forms chiefly rhombohedral (Kenngott, *Sitz. W.* 13, 469); Nordenskiöld (*P.* 96, 100) observed monoclinic crystals in graphite from Finland. H.C. [C,O²] = 96,960 for amorphous C (*Th.* 1, 411); 93,350 for diamond, and 93,560 for graphite (Favre a. Silbermann, *A. Ch.* [3] 33, 411). Emission-spectrum observed by passing sparks through pure CO or CO_2 is characterised by a double line 6583 and 6577·5, three sharp lines 5150·5, 5144·2, 5133, and a band 1266 (Ångström a. Thalén, *Nov. Act. Ups.* 9 [1875]). Besides these, and many other less marked, lines, Liveing a. Dewar describe the arc-spectrum as showing the following marked lines, 3919·3, 2837·2, 2836·3, 2511·9, 2509·9, 2296·5 (*Pr.* 30, 152, 494; 33, 403; 34, 123, 418). A very different spectrum—the band-spectrum is observed at the base of a candle or gas flame, also in cyanogen burnt in O, or by passing sparks through CN, CO at increased pressure, CS_2, &c.; the most characteristic band are 5633, 5164, and 4736. There has been much discussion as to whether this spectrum is that of C or of a hydrocarbon (*v. B. A.* 1880. 264). Three allotropic forms of carbon are known; diamond, graphite, and amorphous carbon.

The diamond was regarded by Newton as a combustible body because of its high refractive power; in 1694 diamond was burnt by the Florentine Academicians; Lavoisier found that CO_2 is produced when diamond is burnt, and Davy showed that diamond is pure carbon. Lavoisier, about 1780, recognised that carbonic acid (then called fixed air) was a compound of O and the element which is the essential element of coal; to this element he gave the name *carbone.* Graphite was long considered to be a kind of lead; Scheele, in 1799, showed it to be closely related to coal; he regarded it as a compound of iron and carbon, but Kastner proved that the iron found in graphite was only an impurity, and that pure graphite is a form of carbon.

Occurrence.—Carbon occurs as diamond and graphite, the former is pure, the latter sometimes approximately pure, carbon; many compounds of C occur in nature; the chief are CO_2 in the air and all waters, mineral carbonates *e.g.* of Ca and Mg, and compounds with H, O, N, and sometimes P and S, in all animal and vegetable organisms. Diamonds are found in India, Borneo, Brazil, the Cape, &c.; graphite, in Cumberland, California, Siberia, &c. Berthelot (*C. R.* 73, 494) found graphite in a meteorite which fell near Melbourne (Australia); and Fletcher found a cubic form of graphite in a meteorite from Western Australia (*Mineralog. Mag.*, Jan. 1887). Graphite is found both amorphous and *foliated.* Coal, anthracite, peat, &c., contain from 50 to 95 p.c. of carbon.

Formation.—Many attempts have been made to form diamond; none has been certainly successful (*v.* Liebig, *Agriculturchemie* [1840] 285; Wilson, *J.* 1850. 697; Favre, *J.* 1856. 828 [from CCl_4]; Despretz, *C. R.* 37, 369 [electric current for a month from Pt to C pole]; Simmler, *P.* 105, 466 [crystallisation from liquid CO_2]; Lionnet, *C. R.* 63, 213 [from CS_2]; Chancourtois, *C. C.* 1866. 1037 [oxidation of hydrocarbon]; Rossi, *C. R.* 63, 408; Hannay, *Pr.* 30, 188 a. 450 [action of Mg, and Li, on gaseous hydrocarbons mixed with N-containing compounds at very high temperatures and pressures]; Marsden, *Pr. E.* 11, 20 [by dissolving amorphous C in molten Ag]). Graphite is formed:—1. By heating charcoal with molten iron, and dissolving out the Fe by HCl and HNO_3Aq.—2. By the slow decomposition of HCNAq, and boiling the product with HNO_3Aq (Wagner, *J. C. T.* 1869. 230).—3. By evaporating the mother liquors obtained in making soda; these contain CN compounds which are decomposed at a certain concentration of the liquid with formation of NH_3, and graphite (Pauli, *D. P. J.* 161, 129; Schaffner, *W. J.* 1869. 250).—4. By leading CO over Fe_2O_3 at 300°-400° (Grüner, *C. R.* 73, 28; Stingl, *B.* 6, 392). Amorphous C is also formed (Berthelot, *C. R.* 73, 494).—5. By the decomposition of CS_2 at high temperatures. 6. By leading CCl_4 over molten pig-iron (Deville, *A. Ch.* [3] 49, 72). Amorphous carbon is formed in many ways:—1. By heating wood, coal, or almost any animal or vegetable matter, out of contact with air, to a high temperature.—2. By the incomplete combustion of wax, tallow, oil, or other combustible compounds of C and H.—3. By decomposing, at a very high temperature and out of contact with air, the gaseous C compounds obtained in the production of gas from coal: the carbon thus obtained is very hard (*v. Properties*).

Preparation.—Pure graphite is obtained by intimately mixing 14 parts of finely powdered foliated graphite with 1 part $KClO_3$ and 2 parts conc. H_2SO_4, heating on the water-bath so long as Cl comes off, washing repeatedly with hot water drying and heating to remove H_2SO_4: if the graphite contains silica it is treated with NaF and H_2SO_4, besides treatment with $KClO_3$ and H_2SO_4 (Brodie, *T.* 1860. 1; *v.* also Winckler, *J. pr.* 98, 243; Stingl, *B.* 6, 391).

Amorphous carbon is prepared approximately pure by strongly heating cane sugar in a closed Pt crucible, boiling the charcoal thus produced with (1) conc. HClAq, (2) KOHAq, (3) water, drying, heating to full redness in a stream of dry Cl and allowing to cool in the same; H is removed as HCl, O as CO, also traces of SiO_2, Fe_2O_3, &c. as $SiCl_4$, Fe_2Cl_6, Al_2Cl_6, &c. The soot from semi-burnt turpentine oil, after treatment with ether, and heating to a high temperature in a closed vessel, is approximately pure carbon. It seems to be impossible to obtain finely divided amorphous C quite free from gases

such as H, O, or Cl; even when purified as described it retains traces of Cl, this may be removed by strongly heating in connection with a Sprengel pump, but on exposure to the air considerable quantities of O, CO_2, &c. are quickly absorbed. The absorbed gases cannot be removed by heating at ordinary pressures; Erdmann a. Marchand (*J. pr.* 23, 159) found ·2 p.c. H and ·5 p.c. O in sugar-charcoal which had been heated nearly to whiteness for 3 hours. According to Porcher (*C. N.* 44, 203) amorphous C free from H, O, and N is obtained by passing CCl_4 vapour over hot pure Na in a hard glass tube, and then heating the C obtained to a little under the temperature at which burning begins. A very hard kind of amorphous carbon is formed by placing wood (box, ash, elder, lilac, or oak), or flax, hemp, cotton, paper, or silk, in a porcelain tube, driving out all air by CS_2 vapour and then gradually heating to redness for an hour (Sidot, *C. R.* 70, 605). The harder the wood and the higher the temperature to which it is heated, the harder and denser is the carbon produced. Various materials consisting mainly of carbon are prepared for industrial use; *charcoal*, by partially burning piles of wood covered with turf or earth, or by the dry distillation of wood; *coke*, by heating coal in iron retorts arranged so that the liquid and gaseous products may be separated from the residual carbonaceous matter; *lamp black*, by partially burning tallow, turpentine, &c., and condensing the soot on cold surfaces; *animal char* (which however contains only about 10–20 p.c. C) by heating bones in closed vessels.

Properties.—Unchanged by action of acids; has not been melted or vaporised.

Diamond is a colourless, transparent, very refractive and dispersive, crystalline, solid; some diamonds are coloured yellow, brown, blue, or black. Diamond is the hardest substance known, but rather brittle; very bad conductor of electricity and heat. C.E. small, especially at low temperatures, at $-42° = 0$. Unchanged by heating out of contact with air to 1300°–1400°; but placed between the carbon poles of a powerful battery it glows brilliantly, swells up, splits, and after cooling the surface resembles coke from bituminous coal (*comp.* Rose, *P.* 168, 497; v. Schrötter, *Sitz. W.* [2] 63, 462; Morren, *C. R.* 70, 990; Jacquelain, *A.* 64, 256; Gassiot, *Ph. C.* 1850. 893; Baumhauer, *Ar. N.* 8, 1). Unchanged when heated to whiteness in water-vapour (Baumhauer, *l.c.*). Strongly heated in a stream of O, diamond is completely burnt to CO_2; it may also be burnt by heating with molten KNO_3; or, very slowly, by powdering finely and heating with $K_2Cr_2O_7$, H_2SO_4, and a little H_2O (Rogers, *J. pr.* 50, 411).

Graphite occurs native both crystalline (*foliated*) and amorphous; it forms a grey, metal-like, hard, opaque, solid; fair conductor of electricity, especially after purification by $KClO_3$, &c. (*v. supra*); fair conductor of heat; is not changed by heating out of contact with air; burns in O to CO_2 at a high temperature, but more slowly than diamond; burnt to CO_2, more easily than diamond, by molten KNO_3, or by $K_2Cr_2O_7$ and H_2SO_4Aq; also by heating with various metallic oxides. When graphite is heated with $KClO_3$ and HNO_3Aq a compound of C, H, and O is formed, called by Brodie *graphitic acid* (probably $C_{11}H_4O_5$); this body is not obtained from diamond or amorphous carbon (*v. Reactions*, No. 9).

The graphite-like form of coke which is formed in the upper parts of the retorts in which coal is heated for gas-making, or is obtained by passing hydrocarbon vapours through red-hot porcelain or iron tubes, is an extremely hard, metal-like, lustrous, sonorous solid; S.G. (2·356) nearly same as that of graphite; it is a good conductor of electricity and a fair conductor of heat; burns with difficulty; it contains no H, and leaves only from ·2 to ·3 p.c. ash (Marchand a. Meyer).

Amorphous carbon (sugar-charcoal; lamp-black) is a dense, black, powder; it is extremely slowly acted on by any reagents, even energetic oxidisers; non-conductor of electricity. The harder forms of amorphous carbon, obtained by calcining hard woods at high temperatures out of contact with air, somewhat resemble graphite in appearance, they are more or less lustrous, conduct electricity fairly well, and burn slowly when heated in air or O. Ordinary amorphous C, or ordinary wood charcoal, absorbs large volumes of gases: Saussure (*G. A.* 47, 113) gives the following volumes absorbed by 1 vol. box-charcoal at 12° and 724 mm.: NH_3 90, HCl 85, SO_2 65, H_2S 55, N_2O 40, CO_2 35, CO 9·4, C_2H_4 35, O 9·2, N 7·5, H 1·75. Hunter (*P. M.* [4] 29, 116; *C. J.* [2] 3, 285; 5, 160; 6, 186; 8, 73; 9, 76; 10, 649) gives these numbers for 1 volume cocoa-nut charcoal at 0° and 760 mm.: NH_3 171·7, CN 107·5, NO 80·3, CH_3Cl 76·4, $(CH_3)_2O$ 76·2, C_2H_4 74·7, N_2O 70·5, PH_3 69·1, CO_2 67·7, CO 21·2, O 17·9. According to Angus Smith (*Pr.* 28, 322) absorption of gases by charcoal takes place in definite volumes; thus if the vol. of H absorbed under definite conditions is 1, the vol. of O = 8, CO = 6, CO_2 = 22, N = 4·66. Chemical reaction sometimes occurs between gases absorbed by charcoal; thus, HCl is produced by leading H over charcoal which has absorbed Cl, and SO_2Cl_2 by leading SO_2 over charcoal under the same conditions. The absorbed gases are removed *in vacuo*. Recently heated porous wood charcoal removes many colouring matters, *e.g.* indigo, from solutions; it also removes fusel oil from weak alcohol, alkaloids from aqueous solutions, many metallic salts from solutions, &c.; in some cases chemical change is produced, *e.g.* $CuSO_4Aq$ and $AgNO_3Aq$ are reduced with pps. of Cu and Ag (Monde, *J. pr.* 67, 255; *v.* also Graham a. Hofmann, *A.* 83, 39; Graham, *P.* 19, 139; Weppen, *A.* 55, 241; 59, 354; Favre, *A. Ch.* [5] 1, 209; Guthe a. Harms, *Ar. Ph.* 69, 121; Stenhouse, *A.* 90, 186).

Specific heat of carbon.—The following numbers summarise the chief determinations exclusive of those of Weber: the temperature-interval is about 35°–55°:—

Diamond: ·143 Bettendorff a. Wüllner (*P.* 133, 293); ·147 Regnault (*A. Ch.* [3] 1, 202); ·366 [20°–1,000°] Dewar (*P. M.* [4] 44, 461).

Gas carbon: ·165 Kopp (*A.* 126, 362; *Supplbd.* 3, 1 a. 289); ·186 B. a. W. (*l.c.*); ·197 R. (*l.c.*); ·32 [20°–1,000°] D. (*l.c.*).

Graphite: ·174 Kopp (*l.c.*); ·188 B. a. W. (*l.c.*); ·201 R. (*l.c.*).

Wood charcoal: ·241 R. (*l.c.*).

In 1874 Weber made careful determinations of the S.H. of the different forms of carbon at different temperatures; he used (1) diamond, (2) native graphite, (3) porous wood-charcoal in a slender filament strongly heated in dry Cl and sealed at once in a glass tube. His chief results were as follows (*v. P.M.* [4] 49, 161 a. 276):—

Diamond.

Temp.	−50°	+10°	85°	250°	606°	985°
S.H.	·0635	·1128	·1765	·3026	·4408	·4529

Graphite.

Temp.	−50°	+10°	61°	201°	250°	641°	978°
S.H.	·1138	·1604	·199	·2966	·325	·4454	·467

Wood Charcoal.

Temp.	0°−23°	0°−99°	0°−223°
S.H.	·1653	·1935	·2385

These numbers show that the S.H. increases as temp. increases, but that the rate of this increase is much smaller at high than at low temperatures. From 600° onwards the S.H. of diamond is the same as that of graphite; as the values for wood charcoal are nearly the same as those for graphite for the same temperature-intervals, the conclusions may fairly be drawn that at temperatures above 600° the different forms of carbon have all the same S.H., and that at lower temperatures there are two values for the S.H., one belonging to graphite and amorphous C, the other to diamond.

Allotropy of carbon. Carbon exhibits allotropic changes in a marked way; diamond may be, superficially at any rate, changed to graphite; amorphous C may also be changed to graphite; each of the three varieties is characterised by special properties. The S.G. of each is characteristic. The heats of combustion (*v. supra*) are different. The S.H.s are not the same; but Weber's results tend to show that, as regards S.H., there is but one form of C existing at temperatures above 600°. Amorphous C remained unchanged when subjected to a pressure of 6,000 7,000 atmos. (Spring, *A. Ch.* [5] 22, 170). The three forms are clearly distinguished, chemically, by their reactions with $KClO_3$ and HNO_3 (*v. Reactions*, No. 9).

Atomic weight.—Determined (1) by burning diamond in O and weighing the CO_2 produced (Dumas a. Stas, *A. Ch.* [3] 1, 5; Erdmann a. Marchand, *J. pr.* 23, 159; Roscoe, *A. Ch.* [5] 26, 136; Friedel, *Bl.* [2] 41, 100); (2) by heating silver acetate and weighing the Ag (Marignac, *A.* 59, 287); (3) by heating Ag salts (oxalate and acetate) and weighing the Ag and CO_2 formed (Maumené, *A. Ch.* [3] 18, 41). The mean of all the (closely agreeing) results is 11·97 (O = 15·96).

Chemical properties.—The atom of C is tetravalent in gaseous molecules (CH_4, CCl_4, CBr_4, &c.). The atomicity of the molecule of C is unknown, as the element has not been gasified; certain considerations, *e.g.* the increase in S.H. as temperature increases, and perhaps the character of the spectrum, seem to indicate that the molecule of C is probably composed of several atoms.

Carbon is distinctly a non-metallic element; it does not replace the H of acids to form salts; it forms stable, but easily gasified, compounds with the halogens; its oxides, and also the sulphide CS_2, are distinctly acidic in their reactions; it exhibits allotropy in a most decided way; the spectrum of C is very complex; yet in some of the physical properties of graphite and dense amorphous carbon, this element approaches the metals (*v. supra*). Carbon stands at the beginning of Group IV. in the periodic classification of the elements; the other members of this group, except Si, are more metallic than non-metallic; C shows closer relations to Si, the first odd-series member of the group, than to any other element in the group (*v.* CARBON GROUP OF ELEMENTS). Both elements are remarkable for the great number of compounds which they form with H, O, and N. Most of the elements of Group IV. except C, form characteristic compounds with F, or double compounds with F and other elements.

Reactions.—1. Unchanged by action of *acids*. 2. *Heat*, in absence of air, produces no change (*comp. Properties of Diamond*). — 3. When strongly *heated in excess of oxygen*, CO_2 is formed: the combination is much retarded if the C and O are carefully dried (Baker, *C. J.* 47, 349).—4. Heated with *sulphuric acid and potassium dichromate* C is slowly burnt to CO_2. 5. Oxidised to CO_2 by heating with molten *nitrate* or *chlorate of potassium*.—6. Reacts with *sulphur vapour* at high temperatures to form CS_2.—7. Combines with *hydrogen* to form C_2H_2; by passing electric sparks between C poles in atmosphere of H.—8. Combines indirectly with *nitrogen* to form cyanogen.—9. Graphite is oxidised by *potassium chlorate and nitric acid* to graphitic acid (?$C_{11}H_4O_5$ or $C_{11}H_4O_6$). Brodie (*T.* 1859. 249) heated an intimate mixture of 1 part purified and very finely divided graphite and 3 parts $KClO_3$, with enough very conc. HNO_3Aq to bring all into solution, at 60° for 3-4 days, until yellow vapour ceased to come off; the contents of the retort were then poured into much water; the insoluble matter was thoroughly washed by decantation, dried on a water-bath, and again oxidised by $KClO_3$ and HNO_3Aq, as before. These operations were repeated (usually 4 times) until no further change was produced, and the insoluble matter formed a clear-yellow solid. Analysis of this yellow solid, dried at 100°, gave the formula $C_{11}H_4O_5$. This body—called *graphitic acid* by Brodie — forms small, transparent, lustrous, yellow plates; it is slightly soluble in water; insoluble in water containing acids or salts; turns blue litmus slightly red; shaken with solutions of alkaline bases it appears to form insoluble salts, but the composition of these is very uncertain; when heated it burns explosively, leaving a fine, black residue; it is easily decomposed by reducing agents such as $(NH_4)HS$, $SnCl_2$, HIAq, &c. (*v. infra*). Brodie supposed this body to be a compound of a hypothetical element which he called *graphon*, and to which he gave the atomic weight 33; he formulated *graphitic acid* as $Gr_4H_4O_5$, and regarded it as the carbon analogue of a silicic acid $Si_4H_4O_5$ obtained by Wöhler from graphitoidal silicon. Gottschalk (*J. pr.* 95, 321) placed a very intimate mixture of 1 part (50 grms.) purified, very finely divided graphite with 3 parts $KClO_3$ in a large flask surrounded by ice-cold water, and very

slowly added enough HNO_3Aq, S.G. 1·525, to completely moisten the whole; he then digested at 50° to 60°, and then at 60° to 70°, for 25–30 hours; he poured off the greater part of the acid and dissolved KNO_3, washed with hot water by decantation, dried *in vacuo* and then at 100°; he repeated this treatment 5 or 6 times; finally he washed the residue with HNO_3Aq S.G. 1·28, removed the acid by pressing between paper and then by washing with alcohol, washed with ether to remove alcohol, pressed again, and dried on the water-bath in the dark. Gottschalk's analyses lead to the formula $C_{11}H_4O_6$ for graphitic acid; he describes a salt, $C_{22}H_{10}K_2O_{12}$, obtained by treating with conc. $KOHAq$ and washing with cold water.

The action of $KClO_3$ and HNO_3 on graphite has also been investigated by Stingl (*B.* 6, 391), and by Berthelot (*A. Ch.* [4] 19, 399). Berthelot calls the compound produced as described *graphitic oxide*, he says it does not react as an acid; he calls the carbon-like mass left on heating graphitic oxide *pyrographitic oxide*; the body is completely dissolved by heating with $KClO_3$ and HNO_3. The porous, amorphous, insoluble body obtained by heating 1 part graphitic oxide with 20 parts HIAq S.G. 2·0 to 280°, Berthelot calls *hydrographitic oxide*; this body is not explosively decomposed by heating, treated with $KClO_3$ and HNO_3 it yields graphitic oxide. There appear to be differences between the *graphitic acids* obtained from different kinds of graphite. Berthelot distinguishes the three allotropic forms of carbon by their reactions with $KClO_3$ and conc. HNO_3; amorphous carbon is oxidised to brown humus-like bodies, which dissolve in water; graphite forms graphitic acid; diamond is unchanged.—10. Both graphite and amorphous carbon are said to yield mellitic acid $C_6(CO_2H)_6$ by the action of $K_2Mn_2O_8$ in $KOHAq$ (Schulze, *B.* 4, 802).—11. Carbon combines with many *metals* when strongly heated with them, *e.g.* with Fe, Ni, Co, &c.; none of these carbides has been isolated as a pure compound (*v.* CARBIDES).

Carbon, halogen compounds of. Carbon does not combine directly with the halogens. These compounds are represented by the formulæ CX_4, C_2X_6, and C_2X_4, where X = Br or Cl; when X = I only CX_4 is known: no fluoride of C has been isolated. The chlorides have been gasified and V.D. of each determined; the formulæ are therefore molecular. The bromides decompose, partially or wholly, when heated: the formulæ are probably molecular. The iodide is easily separated by heat into C and I. The methods of preparation, and reactions, of the chlorides and bromides are very similar. $[C,Cl^4] = 21,030$; $[C^2,Cl^4] = -1,150$ (at const. press. Thomsen). Besides these compounds, several bromochlorides of carbon exist; $CBrCl_3$; two isomeric $C_2Br_2Cl_4$, $C_2Br_4Cl_2$, C_2Br_5Cl, $C_2Br_2Cl_2$, C_2Br_3Cl. [For more details of the halogen compounds of carbon *v.* the *halogen derivatives* of ETHANE, ETHYLENE, and METHANE.]

CARBON BROMIDES. *Carbon dibromide* C_2Br_4 (*Tetrabromethylene*). White crystals; M.P. 53°; produced by heating C_2Br_6, or better, by reducing C_2Br_6 with Zn and H_2SO_4Aq; also by reacting with Br on alcohol or ether, adding $KOHAq$ to remove HBr, and distilling; or by treating $C_2HBr_3.Br_2$ with alcoholic KOH (Lennox, *C. J.* 14, 209). Decomposed by hot Zn, Cu, Fe, ZnO, CuO, &c., giving metallic bromide and C or CO_2 (Löwig, *A.* 3, 292).

Carbon tribromide C_2Br_6 (*Hexabromide Tetrabromethylene dibromide*). Hard, rectangular prisms, easily soluble in CS_2, insoluble in alcohol or ether; decomposed to C_2Br_4 and Br_2 at 200°. Produced by brominating $C_2H_4Br_2$, and by heating C_2HBr_3 with Br and H_2O to 170°–180° (Reboul, *A.* 124, 271).

Carbon tetrabromide CBr_4 (*Tetrabromo-methane*). White lustrous tables; S.G. 3·42; M.P. 91°. B.P. 189·5° (at 760 mm.) with partial decomposition. Insol. in water, very sol. in alcohol, ether, or $CHCl_3$. Partially decomposed with liberation of Br, at 200°; with alcohol at 100° gives HBr, $CHBr_3$, and $CH_3.CHO$; with alcoholic NH_3 at 100° gives $CHBr_3$ and a little guanidine. Formed by the reaction between (1) Br, in presence of I or $SbBr_3$, and $CHBr_3$ or CS_2 or $CBr_3(NO_2)$; (2) Br, in presence of I, and $CHCl_3$. Best prepared by heating 1 part CS_2 with 1½ parts I and 7 parts Br to 150°–160° for 48 hours in a closed tube, shaking contents of tube with NaOHAq, distilling in steam, pressing between paper, and crystallising from alcohol (Bolas a. Groves, *C. J.* [2] 8, 161; 9, 773).

CARBON CHLORIDES. *Carbon dichloride* C_2Cl_4 (*Tetrachlorethylene*). Colourless liquid; ethereal odour; S.G. at 10° 1·62 (R.), 1·612 (G.); S.G. at 0° 1·6595 (B.). B.P. 122° (R.), 116·7° (G.), 121° (B.). V.D. 5·82. Easily combines with Cl in sunlight forming C_2Cl_6. Prepared by reducing C_2Cl_6; C_2Cl_6 is placed in a flask with water and Zn, H_2SO_4Aq is added from time to time, the flask being kept cold and frequently shaken; the C_2Cl_4 is distilled over in steam, dried, and fractionated (Faraday, *T.* 1821. 47; Regnault, *A. Ch.* 71, 377; Geuther, *A.* 107, 212; Bourgoin, *Bl.* 23, 344).

Carbon trichloride C_2Cl_6 (*Tetrachlorethylene dichloride. Carbon hexachloride*). Hard, colourless, rhombic prisms; S.G. 2·0. M.P. 187° and B.P. the same (Städel a. Hahn, *B.* 9, 1735). V.D. 8·15. Insol. in H_2O, sol. in alcohol or ether. Easily reduced, *e.g.* by Zn and H_2SO_4Aq, or by alcoholic KHS, to C_2Cl_4; with $KOHAq$ at 200° gives KCl, H_2O, and $K_2C_2O_4$. Prepared by leading Cl into boiling $C_2H_4Cl_2$ till saturated, cooling by ice, pressing between paper, dissolving in alcohol, ppg. by H_2O, pressing, and crystallising from alcohol (Faraday, *T.* 1821. 47; Regnault, *A. Ch.* 69, 165; 71, 371; Liebig, *A.* 1, 219; Geuther, *A.* 60, 247; Berthelot, *A.* 109, 118).

Carbon tetrachloride CCl_4 (*Tetrachloro-methane*). Colourless liquid, with ethereal odour; S.G. $\frac{0°}{4°}$ 1·63195; B.P. 76·74° (Thorpe, *C. J.* 37, 199). V.D. 5·24. Prepared by leading dry Cl into boiling $CHCl_3$ containing a little $SbCl_3$ or ICl, in a large flask with inverted condenser, removing excess of Cl by shaking with Hg, and fractionating. Also by passing CS_2 and Cl through a hot porcelain tube (Kolbe, *A.* 45, 41; 54, 146). Unchanged by KOHAq; with alcoholic KOH slowly gives KCl, K_2CO_3, and H_2O; passed through a hot tube gives C_2Cl_4, C_2Cl_6, and C; heated with SO_3 gives $COCl_2$ and $S_2O_5Cl_2$; with P_2O_5 gives $POCl_3$ and $COCl_2$

(Regnault, *A. Ch.* 71, 377; Dumas, *A. Ch.* 73, 95).

CARBON IODIDE. CI_4. Dark red octahedra; S.G. $\frac{20°}{}$ 4·32; sol. in alcohol, ether, or CS_2. Decomposed by heat to C and I; boiled with H_2O or dilute HIAq gives CHI_3. Prepared by mixing equal vols. CCl_4 and CS_2 with saturated solution of Al_2I_6 in CS_2, then diluting with H_2O out of contact with air. The solution of Al_2I_6 is prepared by placing the proper quantities of Al (in small pieces) and I in a stoppered flask and adding 3 times the quantity of CS_2 (Gustavson *B.* 14, 1705).

CARBON BROMOCHLORIDES: *Trichlorobromo-methane* CCl_3Br; two *tetrachlorodibromo-ethanes* $C_2Cl_4Br_2$; *dichlorotetrabromo-ethane* $C_2Cl_2Br_4$; *chloropentabromo-ethane* C_2ClBr_5; *dichlorodibromo-ethylene* $C_2Cl_2Br_2$; *chlorotribromo-ethylene* C_2ClBr_3 (*v.* these compounds under METHANE, ETHANE, and ETHYLENE).

Carbon, hydrate of (?) By treating pig-iron with (1) $CuSO_4Aq$, (2) Fe_2Cl_6Aq containing HCl, a brownish-black substance remains, containing, according to Schützenberger a. Bourgeois (*C. R.* 80, 911) carbon and water in the ratio $11C:3H_2O$. Besides the C and H_2O, the substance gives about 10 p.c. ash. It loses $3H_2O$ at 250°.

Carbon nitride = CYANOGEN (*q. v.*).

Carbon, oxides of. Two oxides certainly exist, CO and CO_2; these formulæ are molecular; each bears the relation of anhydride to an acid, CO is formic anhydride (the acid is H_2CO_2), CO_2 is carbonic anhydride (the acid is H_2CO_3) (*v. infra*). Both oxides can be obtained by direct combination of O with C; either can be produced from the other, by combining with O or with C, respectively. Both are stable gases; CO is an energetic reducer; CO_2 in a few cases acts as an oxidiser. Brodie (*Pr.* 21, 245) and Berthelot (*Bl.* [2] 21, 102) have described bodies, produced by the induced electric discharge on CO, as oxides of C. Brodie noticed a gradual diminution in vol. of the CO and the formation of a red-brown film on the glass tube; the solid was soluble in water giving a markedly acid solution; its composition appeared to differ in different experiments; Brodie gives the formulæ C_4O_3 and C_5O_4. Berthelot got brown, amorphous, humus-like bodies which dissolved in water with acid reactions, gave brown pps. with $AgNO_3Aq$, BaOAq, and $Pb2NO_3Aq$; at 300°-400° CO and CO_2 (equal vols.) were evolved, and another dark body remained, to which B. gave the composition C_8O_3. B. also (*A. Ch.* [5] 17, 142) states that by the action of electric sparks on pure CO_2 a gas was produced which reacted violently with Hg and oxidisable bodies.

CARBON MONOXIDE. CO. (*Carbonic oxide*; more properly, although rarely, *carbonous oxide*; *formic anhydride*.) Mol. w. 27·93. S.G. ·9678 (air = 1). V.D. 14. (c. −186°) (Wroblewski, *C. R.* 98, 982). S.H. p. ·2346. S.H. v. ·16844 (E. Wiedemann, *P.* 157, 1). S.E. ·003667 (Regnault). S. (6°) ·0287; (9°) ·0269; (13·5°) ·02315 (Bunsen). S. alcohol (2°) ·20356; (13°) ·20416; (16°) ·20566; (24°) ·20452 (Bunsen). $\mu_D = 1·000301$; $\mu_E = 1·000350$; $\mu_G = 1·000391$ (Croullebois, *A. Ch.* [4] 20, 136). [CO, O] = 67,960 at const. press., and 67,670 at const. vol.; [C,O] = 29,000, and 29,290, respectively (Thomsen). Does not exactly obey Boyle's law; $\frac{pv}{p_1v_1} = 1·00293$ (Regnault, *Acad.* 1862. 26, 229). Liquefied by cooling to −136° at pressure of 200–300 atmos. and then decreasing pressure, not too quickly, to not less than 50 atmos. (Wroblewski a. Olszewski, *A. Ch.* [6] 1, 112; *v.* also Natterer, *W. A. B.* 12, 199; and Cailletet, *C. R.* 85, 1213 a. 1217, and *A. Ch.* [5] 15, 132). First obtained in 1776, by Lasonne, by heating C with ZnO; obtained by Priestly, in 1796, by heating charcoal with iron oxide, but supposed by him to be H; proved by Cruickshank not to be a hydrocarbon; true composition determined by Clement and Desormes.

Occurrence.—In the gases from burning coal or charcoal; from the partial combustion or putrefaction of organic matter; or from the reduction of metallic oxides by charcoal, *e.g.* in the blast-furnace (Bareswil, *J. Ph.* [3] 25, 172; Bunsen, *P.* 46, 193; 50, 81). During the oxidation of gallic and tannic acids by exposure to air in alkaline solutions (Boussingault, *A. Ch.* [3] 66, 295; Calvert, *C. R.* 57, 873). In pig-iron and steel according to Troost a. Hautefeuille, also Parry (*J.* 1873. 997; 1874. 1083).

Formation.—1. By passing steam over excess of red-hot C; the product may contain about $28\frac{1}{2}$ p.c. CO, $56\frac{1}{4}$ p.c. H, $14\frac{3}{4}$ p.c. CO_2, and traces of CH_4 (*v.* Naumann a. Pistor, *B.* 18, 164). 2. By passing a slow current of CO_2 over red-hot C, and washing the gases through KOHAq and soda-lime.—3. By heating CO_2 with those metallic oxides which do not readily part with O, *e.g.* ZnO, PbO, Fe_2O_3; oxides which readily give up O yield but little CO, as it is again oxidised to CO_2.—4. By passing CO_2 over red-hot Cu, or over hot Zn-dust (Noack, *B.* 16, 75).—5. By heating CO_2 to 1300° (Deville, *C. R.* 59, 873).—6. By electric sparks through CO_2 (Buff a. Hofmann, *A.* 113, 140).—7. By heating powdered $CaCO_3$ or K_2CO_3 with one-sixth its weight of powdered charcoal; Na_2SO_4 heated with C also yields CO (with Na_2S).—8. In very small quantities (with COS) by passing CO_2 and S vapour through a red-hot tube (Berthelot, *A. Ch.* [5] 30, 547).—9. By heating dry $H_2C_2O_4$, or by reaction between $H_2C_2O_4$ or an oxalate and hot conc. H_2SO_4.—10. By heating $H.CO_2H$, or a formate, with conc. H_2SO_4.

Preparation.—1. One pt. dry powdered $K_4Fe(CN)_6$ is heated, in a capacious vessel, with 8-10 pts. conc. H_2SO_4; as soon as frothing begins the lamp is lowered to a small flame; the gas is passed through milk of lime and KOHAq, to remove CO_2 and the SO_2 formed in the process; SO_2 is evolved only in the earlier stages of the reaction (Grimm a. Ramdohr, *A.* 98, 127). 15 g. $K_4Fe(CN)_6$ yield about 4 litres CO:

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O$$
$$= 6CO + 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 \text{ (Fownes).}$$

2. Dry CaC_2O_4, or BaC_2O_4, is mixed with about $\frac{1}{10}$ pt. dry CaO_2H_2, and the mixture is strongly heated in a hard glass flask; the gas is passed through milk of lime, and is then dried:—CaC_2O_4 gives $CaCO_3 + CO$; the CaH_2O_2 absorbs any CO_2 formed.—3. According to Cherrier (*C. R.* 69, 138) pure CO may be prepared by passing the gases produced by heating $H_2C_2O_4$ with H_2SO_4 through a red-hot tube filled with

charcoal, and then through a mixture of CaOAq and KOHAq.

Properties.—A colourless, tasteless, slightly odorous gas; liquefied at low temperature and great pressure (*v. supra*). CO is combustible but a non-supporter of combustion: the temperature of the flame of CO in air is about 1400° (Valerius, *J.* 1874. 58). Absorbed by C, and by several metals, *e.g.* K, Ag, Au; quickly absorbed by Cu_2Cl_2 in a little HClAq (*v. infra*); decomposed at very high temperature to C and CO_2; decomposed when moist by induction-sparks; CO is an energetic reducer; it combines with moist KOH (or NaOH) to form K formate; combines directly with Cl and Br in sunlight. CO is extremely poisonous; it removes O from the blood and combines with the hæmoglobin. CO may be detected in the blood by observing the absorption-spectrum; this is almost identical with that of oxygenated blood, and is characterised by two bands between D and E; on adding a little ammonium sulphide these bands disappear in the case of oxygenated blood, and the spectrum shows one band midway between D and E; if the blood contains CO the two bands remain unchanged for several days (Vogel, *B.* 11, 235; Hoppe-Seyler, *Fr.* 3, 439).

Reactions.—1. *Electric sparks* cause a partial decomposition to CO_2 and C; if the CO_2 is removed the change proceeds (Berthelot, *A. Ch.* [5] 30, 547). According to Berthelot (*Bl.* [2] 21, 102; *A. Ch.* [5] 17, 142) CO is decomposed by the *induction-discharge*, with production of CO_2 and (?) C_4O_3 and C_5O_4 (*v. ante*; beginning of this art.). According to Buff a. Hofmann (*C. J.* 12, 282) the induction-spark does not decompose dry pure CO. Dixon (*C. J.* 49, 103) found that CO was decomposed (only about $\frac{1}{2}$ p.c. of the total gas) by sparks from a Leyden jar.—2. *Heated* to about 1300° CO is partially decomposed to C and CO_2 (Deville, *C. R.* 59, 873).—3. A mixture of CO with *oxygen* is burnt to CO_2 by application of a flame or electric sparks. Dixon (*T.* 1884. 617) has proved that if both gases are perfectly dry no chemical change occurs when a spark is passed; that a mere trace of steam renders the mixture explosive; that the oxidation of CO by O takes place very slowly if only a *very small* quantity of steam is present; and that as the quantity of steam is increased the rapidity of the explosion is increased also. The steam acts as a carrier of O to the CO; it is probably reduced, and the H is then again oxidised: the reactions which occur are very probably these (*v.* Dixon, *C. J.* 49, 94):

$$\left\{\begin{array}{l}2CO + 2H_2O = 2CO_2 + 2H_2\\ 2H_2 + O_2 = 2H_2O\end{array}\right\}.$$

Or (Armstrong, *C. J.* 49, 112) the changes may be represented by the formulæ, *before explosion* $O.H_2O.CO$; *after explosion* $OH_2.OCO$. Small quantities of gases other than H_2O were tried (H_2S, C_2H_4, H_2CO_2, NH_3, C_5H_{12}, HCl; SO_2, CS_2, CO_2, N_2O, C_2N_2, CCl_4); if the gas contained H, explosion occurred; if the gas did not contain H the mixture did not explode.—4. When a mixture of CO and *steam is heated* to about 600°, a portion of the CO is oxidised to CO_2; the amount of CO oxidised depends on the conditions (*v.* Dixon, *C. J.* 49, 94: references to other memoirs are given); if the CO_2 is removed as it is formed the whole of the CO can be oxidised. L. Meyer's experiments (*B.* 19, 1099), however, seem to prove that a mixture of dry CO and O can be exploded if a very strong spark is used, and the temperature is thus made very high. The gases must be under considerable pressure; the more dilute the gaseous mixture the more difficult is it to explode it.—5. When *sparks from an induction-coil are passed through a mixture of* CO *and steam*, CO_2, a little formic acid, and in some cases C, are formed (Dixon, *C. J.* 49, 94).—6. When to a mixture of *dry* CO *with hydrogen, oxygen in sufficient for complete combustion is added, and the mixture is exploded by the spark*, CO_2 and H_2O are formed; the ratio of CO_2 to H_2O depends on the shape of the vessel, and the pressure up to a certain limit; above this pressure —the 'critical pressure'—the ratio $CO_2:H_2O$ is independent of the shape of the vessel. The larger the quantity of O used the lower is the critical pressure. So long as the volume of H is more than twice that of the O the ratio of $CO \times H_2O:CO_2 \times H_2$ remains constant, provided no H_2O can condense, and the pressure is above the critical pressure: when the vol. of H is less than twice that of O the value of the ratio diminishes. The presence of an inert gas, *e.g.* N, increases the formation of CO_2 and diminishes that of H_2O, hence it lowers the value of the ratio $CO \times H_2O:CO_2 \times H_2$. This ratio is called by Dixon the *co-efficient of affinity* of the reaction (*v.* Dixon, *T.* 1884. 617; *C. J.* 49, 94; Horstmann, *B.* 12, 64; *v.* also CHEMICAL CHANGE).—7. CO is oxidised to CO_2 (1) by *bichrome and sulphuric acid* (Ludvig, *J.* 1872. 248); (2) by *palladium charged with hydrogen, in presence of oxygen and water*, H_2O_2 being also produced (Traube, *B.* 15, 2325, 2854; 16, 123; Remsen a. Keiser, *B.* 17, 83); (3) by *mixing with oxygen and passing over platinum-black*; (4) by *nitrogen dioxide* $[NO_2]$ (Hasenbach, *J. pr.* [2] 4, 1); (5) *by heating with most metallic oxides*; (6) by *heating with many oxysalts, e.g.* alkaline sulphates (sulphides produced).—8. Many experiments have been made to determine whether CO is oxidised by contact with *moist oxygen in presence of slowly oxidising phosphorus*; the balance of evidence seems to show that CO_2 is not produced (Remsen (and others) *Am. S.* [3] 11, 316; *B.* 17, 83; *Am.* 6, 153; Leeds, *B.* 12, 1836; *C. N.* 48, 25; Baumann, *B.* 16, 2146; 17, 283).—9. CO reacts with *moist potash or soda* to form alkali formate (Berthelot, *A. Ch.* [3] 61, 463); the reaction proceeds most quickly at 190°–200°, and is best accomplished by leading moist CO over soda-lime (Fröhlich a. Geuther, *A.* 202, 317).—10. With *ferrous oxide* at 300°–400°, CO_2 and a little C are formed (Grüner, *C. R.* 73, 281).—11. CO appears to react with certain *metallic peroxides* to form carbonates, but, according to Wright a. Luff (*C. J.* 33, 540), CO_2 is formed by partial reduction of the peroxide and reacts with the lower oxide to produce carbonate.—12. Many of the preceding reactions exhibit CO as a *reducing agent*; it also reduces $PdCl_2Aq$ to Pd.—13. When *sodium or potassium is heated to redness in* CO, alkali carbonate and C are formed.

Combinations.—1. With *potassium* at about 80° to form the explosive compound KCO (Brodie, *C. J.* [2] 12, 269), *v.* POTASSIUM.—

2. With *chlorine* or *bromine* in sunlight, to form $COCl_2$, or $COBr_2$ (*v.* CARBON, OXYCHLORIDE, and OXYBROMIDE, OF).—3. With *sulphur* to form COS (*v.* CARBON, OXYSULPHIDE OF).—4. With *platinic chloride* to form $C_3O_3PtCl_4$ and $C_2O_2PtCl_2$ (Schützenberger, *A. Ch.* [4] 21, 350).—5. CO is absorbed by anhydrous HCN (Böttinger, *B.* 10, 1122); by several metals, *e.g.* Fe, Ag, Au; by carbon.—6. CO does *not* combine with cyanogen, nor does it react with $Hg(CN)_2$.

Estimation.—CO in a gaseous mixture is absorbed by Cu_2Cl_2 solution. Thomas (*C. N.* 37, 6) prepares the solution by filling a vessel of 120 c.c. capacity $\frac{2}{3}$ full of Cu turnings, adding 6 g. crystallised $CuCl_2$ and 20 c.c. conc. HClAq, and shaking until solution of the $CuCl_2$ is effected; he then adds 30 c.c. water and shakes briskly for some time, and then adds 30 c.c. water.

CARBON DIOXIDE. CO_2. (*Carbonic anhydride*, often called *carbonic acid.*) Mol. w. 43·89. S.G. gas 1·53; S.G. liquid 1·057 at −34°; 1·016 at −25°; ·966 at −11·5°; ·91 at −1·6°; ·84 at +11°; ·726 at +22·2° (Cailletet a. Mathias, *C. R.* 102, 1202). S.G. solid (hammered) slightly under 1·2 (Landolt, *B.* 17, 309) [−65°] (Mitchell); [−57°] (Faraday); [−78·2°] (Regnault, *A. Ch.* [3] 26, 257). V.D. 22; 22·42 at 800°; 21·2 at 1180° (Meyer a. Goldschmidt, *B.* 15, 1165). S.H.v. ·33 (equal vol. of air = 1), ·2169 (equal weight of air = 1) (Regnault, *C. R.* 36, 676, &c.; *v.* also Wiedemann, *P.* 157, 21). $\frac{\text{S.H.p.}}{\text{S.H.v.}} = 1·29$ to 1·305 (Amagat, Röntgen, *C. R.* 71, 336; 77, 1325). C.E. ·0037 (Regnault, Magnus, Joly). $\frac{PV}{P_1V_1} = 1·00722$ (Regnault, *C. R.* 20, 975). At 200° CO_2 obeys Boyle's law (Amagat, *C. R.* 68, 1170; 73, 183). C.E. liquid CO_2 very large, 120 vols. at −20° become 150 vols. at +30, (Thilorier, *A. Ch.* 60, 427). Critical temperature = 30·9° (Andrews, *T.* 1869. 575). Vapour-pressure of liquid CO_2 (Regnault) in atmospheres: −25°, 17·1; −5°, 30·9; 0°, 35·4; +5°, 40·5; 15°, 52·2; 25°, 66; 35°, 82·2; 45°, 100·4. Vapour-pressure of solid CO_2 (Faraday) in atmos.: −57°, 5·33; −70·5°, 2·2; −99·4°, 1·14. B.P. of solid CO_2—*i.e.* temp. at which vapour-pressure = 760 mm.—is much lower than the M.P.; Regnault (and Pouillet) found −78° to −79° (*P.* 77, 107); Thilorier, −95° to −98°; and Faraday, as shown by values for vapour-pressure, under −99°. By evaporation of solid CO_2 mixed with ether, temp. is c. −100°.

S. CO_2 gas (Bunsen, *A.* 93, 1):

At 0°	1·7967	At 11°	1·1416
1	1·7207	12	1·1018
2	1·6481	13	1·0653
3	1·5787	14	1·0321
4	1·5126	15	1·0020
5	1·4497	16	0·9753
6	1·3901	17	0·9519
7	1·3339	18	0·9318
8	1·2809	19	0·9150
9	1·2311	20	0·9014
10	1·1847		

Absorption-coefficient = $1·7967 - ·07761t + ·0016424t^2$.

S. CO_2 gas in alcohol (Bunsen):

At 3·2°	4·0442	At 14·2°	3·2357
6·8	3·7374	18	3·0391
10·4	3·4875	22·6	2·8277

Absorption-coefficient = $4·32955 - ·09395t + ·00124t^2$.

$\mu_G = 1·000395$, $\mu_E = 1·000156$, $\mu_D = 1·000496$ (Croullebois, *A. Ch.* [4] 20, 136; *v.* also Chappuis a. Rivière, *C. R.* 103, 37). H.F.p. [C,O²] = 96,960; [CO,O] = 67,960. H.F.v. [C,O²] = 96,960; [CO,O] = 67,670. [C,O²,Aq] = 102,840. [CO,O,Aq] = 73,840. [CO²,Aq] = 5,880. [CO²Aq,nNaOHAq]; n = 1 = 11,016; n = 2 = 20,184; n = 4 = 20,592 (Thomsen).

Carbon dioxide has been known for centuries. The identity of the gases produced during fermentation and by the action of acids on chalk was established by Black. Bergmann recognised the same gas in the atmosphere. Cavendish proved that the same gas was produced by burning charcoal. Lavoisier established the composition of the gas. Faraday liquefied, and Thilorier solidified, carbon dioxide.

Occurrence.—In the atmosphere (*v.* ATMOSPHERE); in mineral waters; issues from the earth in different places; sometimes found liquid in cavities in quartz, &c. Produced by the breathing of animals, by the decay of organic matter, by the combustion of coal, charcoal, &c. In combination as carbonate, of calcium, magnesium, &c., &c.

Formation.—1. By burning C in air or O.—2. By oxidation of most C-compounds.—3. By burning CO.—4. By reducing many metallic oxides by C.—5. By heating together H_2O and CO.—6. By the reaction between red hot C and steam.—7. By the action of steam on $CaCO_3$ at red heat.—8. By heating a mixture of $K_2Cr_2O_7$ with Na_2CO_3.—9. By heating several carbonates. 10. During fermentation. −11. By reaction between acids and carbonates.

Preparation.—$CaCO_3$ or $MgCO_3$ in lumps is treated with dilute HClAq at the ordinary temperature; the gas is passed through $NaHCO_3Aq$ (to remove HCl which may have passed over), and is then dried by $CaCl_2$. Bunsen recommends the use of finely powdered chalk and conc. H_2SO_4, and addition of a very little water.

Liquid carbon dioxide was obtained by Faraday by decomposing $(NH_4)_2CO_3$ by H_2SO_4Aq in one limb of closed glass tube bent at an obtuse angle. Thilorier (*A. Ch.* 60, 247) decomposes $NaHCO_3$ by dilute H_2SO_4Aq in an iron vessel connected with an iron cylinder in which the CO_2 is liquefied by its own pressure. Natterer (*J. pr.* 35, 169) compresses CO_2 by a specially constructed air-pump (*v.* also Gore, *T.* 1861. 63).

Solid carbon dioxide is obtained by allowing the liquid to escape into a tin vessel; part of the liquid becomes gas and part is solidified. Landolt allows the liquid to evaporate freely into conical woollen bags; he then compresses the solid CO_2 in conical moulds of hard wood by wooden pistons (*B.* 17, 309).

Properties.—A heavy, colourless, gas; incombustible; non-supporter of ordinary combustion, but strongly heated K or Na, or brightly burning Mg, burns in CO_2. Absorbed by water, solution colours litmus wine-red and reacts as

a weak acid (v. Carbonic acid). Absorbed by moist alkalis and alkaline earths forming carbonates; rapidly absorbed by mixture of powdered KOH and hydrated Na_2SO_4. Poisonous, by cutting off supply of O.

Liquid carbon dioxide is a limpid, colourless, refractive, liquid; nonconductor of electricity; not changed by strong induction-sparks; very expansible by heat; C.E. is greater than that of the gas. Insol. in water which swims on the surface; mixes with alcohol, ether, &c. Does not dissolve S or P; dissolves I; no reaction with Na or K (Cailletet, *C. R.* 75, 1271).

Solid carbon dioxide is a white, loose, snow-like, solid; when compressed by hammering in wooden moulds it resembles chalk (Landolt, *B.* 17, 309). Very bad conductor of heat. Evaporates slowly, a specimen prepared by Landolt 53 mm. by 71 mm. diam. took 5 hours to volatilise in the air. Burns, if pressed against the skin.

Reactions.—1. *Heated* to c. 1300° in porcelain tube is partly changed to CO and O (Deville, *C. R.* 56, 729; *v.* also Berthelot, *C. R.* 68, 1035).—2. Partly decomposed by *electric sparks*; a condition of equilibrium is attained when change of CO_2 into CO + O equals that of CO and O into CO_2 (Dixon a. Lowe, *C. J.* 47, 571).—3. *Mixed with hydrogen, and heated to bright redness or submitted to induction-sparks*, H_2O and CO are formed; if H_2O is removed the whole of the CO_2 goes to CO (Dixon, *C. J.* 49, 94). According to Dubrunfaut (*C. R.* 74, 125) CO_2 and H passed over hot pumice give C and H_2O.—4. *A mixture of carbon dioxide and sulphur vapour passed through a red-hot tube* yield a little COS, CO, and SO_2 (Berthelot, *Bl.* [2] 40, 362).—5. With *sulphuretted hydrogen, passed through red-hot tube*, forms CO, H_2O and S (Köhler, *B.* 11, 205).—6. Decomposed by *chlorophyll*-parts of plants in sunshine.—7. Reduced to CO by heating with *carbon, iron* or *zinc*, or with *copper* which has occluded hydrogen (Tissandier, *C. R.* 74, 531; Schrötter, *W. A. B.* 34, 27).—8. Partly reduced to CO by reaction with *ferrous sulphate and a little water*, in a closed tube (Horsford, *B.* 6, 1390).—9. Reduced to C by heating strongly with *sodium, potassium*, or *magnesium; alkali carbonates strongly heated with phosphorus or boron* give CO_2 which is reduced to C (Tennant, *Crellis A.* [1793] 1, 158; Dragendorff, *J.* 1861. 111; Leeds, *B.* 12, 1834 a. 2131).—10. With moist *alkalis*, or *alkaline earths*, forms carbonates.—11. With *water* probably forms a solution of carbonic acid, H_2CO_3 (*v.* Carbonic acid).—12. With *sodium- or potassium-amalgam* at c. 350° gives Na (or K) oxalate (Drechsel, *A.* 146, 141).—13. With *sodium* CO_2Aq reacts to give Na formate (Kolbe a. Schmitt, *A.* 119, 251). 14. Decomposes moist *potassium iodide* at high temperature giving HI (Papasogli, *G.* 1881. 227).

Carbon, oxybromide of. The existence of a Br compound of CO analogous to $COCl_2$ is doubtful. A mixture of Br vapour with excess of CO is slowly, but not fully, decolourised in sunlight; in contact with KOHAq this gas produces KBr and K_2CO_3 (Schiel, *A. Suppl.* 2, 311). Emmerling a. Lengyel could not obtain a trace of any compound of C, Br, and O, by the reaction between COS and Br at a high temperature (*B.* 2, 547). By the reaction between H_2SO_4 (50 parts), $K_2Cr_2O_7$ (20-25 parts), and $CHBr_3$ (5-10 parts), Emmerling (*B.* 13, 874) obtained a small quantity of a liquid, which he slowly distilled through Sb, to remove Br; he thus obtained a colourless heavy liquid, smelling like $COCl_2$. The B.P. rose from 12° to 30°; analyses seemed to show that the liquid was a mixture of $COCl_2$ and C oxybromide.

Carbon, oxychloride of. $COCl_2$. (*Carbonyl chloride. Phosgene gas. Chloro-carbonic acid.*) Mol. w. 98·67. (8·2° at 756 mm.). S.G. $\frac{0°}{4}$ (liquid) 1·432; $\frac{18.6°}{4}$ 1·392 (Emmerling a. Lengyel, *A. Suppl.* 7, 101). V.D. 50·6 (E. a. L.). $[C,O,Cl^2]$ = 54,850 at constant volume; 55,140 at constant pressure (Thomsen). First prepared by J. Davy in 1811 (*T.* 1812. 144) by the action of sunlight on Cl + CO (hence the name *phosgene*).

Formation.—1. By leading CO into boiling $SbCl_5$ (Hofmann, *A.* 70, 139; *v.* also Butlerow, *Z.* 1863. 481; Kraut, *Gm.-K.* I. 2, 386), or over hot $PbCl_2$ or AgCl (Göbel, *J. pr.* 6, 388).—2. By heating CCl_4 with ZnO at 200° in a closed tube; or by passing CCl_4 and CO through pumice in a tube heated to about 400°.—3. By heating $CHCl_3$ (1 part), $K_2Cr_2O_7$ (2½ parts), and H_2SO_4 (10 parts) at 100°, and passing the gas over Sb to absorb Cl (E. a. L.).—4. By passing Cl and CO over Pt black at about 400° (Schützenberger, *Bl.* [2] 10, 188; 12, 198).—5. By passing Cl and CO_2 over hot C (Schiel, *J. pr.* 6, 388). (For other methods *v.* Schützenberger, *B.* 2, 218; Dewar a. Cranston, *C. N.* 22, 174; Armstrong, *B.* 3, 730.)

Preparation.—Dry Cl and dry CO are slowly passed through a succession of large bottles freely exposed to sunlight, then through a U-tube loosely filled with pieces of Sb (to remove free Cl), and finally into a tube surrounded by snow and salt. Each gas should pass through the drying-bottles at as nearly as may be the same rate. 100 litres CO give 140-155 g. $COCl_2$ in direct sunlight. Paterno (*G.* 5, 233) passes the mixed gases through a tube 400 mm. long filled with animal charcoal: combination occurs with production of heat; the tube must be cooled by a wet cloth from time to time (*v.* also Wilm a. Wischin, *A.* 147, 150).

Properties.—Colourless gas with penetrating odour; at 8° and under it is a colourless limpid liquid; the gas is soluble in acetic acid, benzene, and several liquid hydrocarbons.

Reactions.—1. *Water* absorbs $COCl_2$ with formation of CO_2Aq and HClAq. Berthelot (*C. R.* 87, 591) gives the value $[COCl^2,Aq]$ = 64,600. 2. *Alcohol* forms *chlorocarbonic ether* CO.Cl.OEt (*q. v.*).—3. Several *metals* decompose $COCl_2$, when heated with it, to CO and metallic chloride; *e.g.* Sb, As, Na, Sn, Zn; *potassium* forms KCl, K_2CO_3, and C.—4. With slightly moist *potassium carbonate*, KCl, H_2O, and CO_2 are formed.—5. *Zinc oxide* produces $ZnCl_2$ and CO_2.—6. Combines with 4 vols. *ammonia* to form urea and NH_4Cl (Natanson, *A.* 98, 288; Fenton, *C. J.* 35, 793).

Carbon, oxysulphide of. COS. (*Carbonyl sulphide.*) Mol. w. 59·91. V.D. 30·4. [CO,S] = 8,030; [C,O,S] = 37,030; $[COS,O^3]$ = 131,010 (Thomsen).

Occurrence.—According to Thom (*A. Suppl.*

5, 236), in several mineral waters, and in volcanic gases.

Formation.—1. By passing CO and S vapour through a red-hot porcelain tube (Thom).—2. By gently heating SO_3 with CS_2; SO_2 and S also produced (Armstrong, *B.* 2, 712).—3. By action of CO_2 on boiling S; or by electric sparks on CO_2 mixed with S vapour (Cossa, *B.* 1, 117; Chevrier, *C. R.* 69, 136).—4. By leading alcohol and CS_2 over red-hot Cu (Carnelley, *C. J.* [2] 13, 523). For other methods v. Ladenburg, *B.* 1, 273; 2, 30, 53, 271; Dewar a. Cranston, *C. N.* 20, 174; Salomon, *J. pr.* [2] 5, 476.

Preparation.—By decomposing KCNS by H_2SO_4Aq; $KCNS + H_2O + 2H_2SO_4Aq = COS + KHSO_4Aq + NH_4HSO_4Aq$. KCNS is added to a cold mixture of 5 vols. H_2SO_4 with 4 vols. H_2O as long as the whole remains liquid; if much gas comes off the vessel is cooled, if very little gas is evolved the vessel is warmed gently. The gas is passed through three U tubes, containing (1) cotton wool charged with moist HgO (to remove HCN and formic acid), (2) cuttings of unvulcanised caoutchouc (to remove CS_2), (3) $CaCl_2$; the gas is then collected over Hg (Thom). Bender (*A.* 148, 137) recommends passing the gas through a tube surrounded by snow and salt, and Hofmann (*B.* 2, 73) through wool moistened with PEt_3; the object in either method being to remove CS_2.

Properties.—Colourless, heavy, gas, with a pleasant somewhat aromatic odour. Colours moist blue litmus slightly reddish. Absorbed by water; solution sometimes contains CO_2 and H_2S. Very sol. in alcohol.

Reactions.—1. *Burns in air* to CO_2 and SO_2.—2. At full *red heat* gives CS_2 and CO_2 (Berthelot, *C. R.* 87, 571).—3. With *water* gives CO_2Aq and H_2SAq.—4. With *potash solution* gives K_2SAq and K_2CO_3Aq; similar reactions with NH_4Aq, CaO_2H_2Aq, and BaOAq.—5. *Ammonia gas*, or alcoholic NH_3, gives $CO.NH_2.SNH_4$ (v. Berthelot, *A. Ch.* [5] 30, 539).—6. Solutions of *salts of copper, cadmium, lead*, or *silver* give no pps., but on adding NH_3Aq the sulphides of the metals are ppd.—7. The gas is decomposed by hot *mercury, copper, silver*, and *iron*, giving sulphides; by hot *sodium*, giving Na_2S, Na_2CO_3, and C.

Carbon selenide. Carbon and selenion do not combine directly. No definite compounds have been isolated. Rathke obtained a liquid which probably contained about 2 p.c. of a selenide of carbon (along with CCl_4), by heating selenide of phosphorus with moist CCl_4 (v. *A.* 152, 181).

Carbon, sulphides of. Carbon disulphide, CS_2, is a well-marked compound. A monosulphide, CS, probably exists. According to Löw a sesquisulphide, C_2S_3, can be obtained by the action of Na amalgam on CS_2 (*Z.* 9, 173; 10, 20). When sodium and CS_2 react a red-brown solid is obtained which according to Raub has the composition C_2S_2 (*C. C.* 1870. 579).

CARBON MONOSULPHIDE. CS. Mol. w. unknown. S.G. 1·66. CS_2 was exposed to sunlight for 2 months in a U tube of special construction; the solid which had formed on the walls of the tube was removed by water, washed with CS_2, and dried in H (Sidot, *C. R.* 69, 1303; 74, 180; 81, 32). CS is a red powder; insol. in water, alcohol, turpentine, and benzene. Somewhat soluble in CS_2 or ether. Dissolved by HNO_3Aq, not by HClAq or H_2SO_4Aq. At 200° gives C and S. Heated with S gives CS_2. CS is *not* produced by leading CS_2 over hot carbon or pumice, by heating Sb_2S_3 with C, by reaction between CO and H_2S_2, by reaction between CO and H_2S, by reaction between CH_4 and SO_2 or S_2Cl_2, by heating $(CN)_2S$, by heating Fe spiral in CS_2, by electric sparks through CS_2, or by reaction between $CSCl_2$ and hot Cu.

References.—Baudrimont, *C. R.* 44, 100; Berthelot, *J.* 1859. 83; Playfair, *C. J.* 13, 248; Buff a. Hofmann, *A.* 113, 129; Hermann, *J. pr.* 79, 448; Husemann, *A.* 117, 229; Kern, *C. N.* 33, 253; Rathke, *A.* 167, 195.

CARBON DISULPHIDE. CS_2. (*Thiocarbonic anhydride. Sulphocarbonic acid.*) Mol. w. 75·93. [c. −12°] (Wartha, *B.* 3, 80). (46·04° at 760 mm.) (Thorpe, *C. J.* 37, 362; references in this paper to other determinations). S.G. $\frac{0°}{4°}$ 1·29215 (T.). V.D. 38. S.H. (liquid; 14°–29°) ·2168 (Schüller, *P. Ergzbd.* 5, 116; v. also Hirn, *A. Ch.* [4] 10, 63 and 91). S.H. p. (equal mass of air = 1) ·1569; (equal vol. of air = 1) ·412 (Regnault). C.E. v. Thorpe (*l.c.*). $[C, S^2]$ const. press. = −26,010; const. vol. = −25,430; liquid = −19,610; $[CS^2, O^6] = 265,130$ (Thomsen). For table of vapour-pressures from 0° to 50° v. Ramsay a. Young, *C. J.* 47, 653. μ_A 1·6059; μ_G 1·6729 (at 13°) (Kundt, *W.* 4, 34). For relations between volume as gas and pressure v. Herwig, *P.* 137, 19; 141, 83; 147, 161.

Occurrence.—In crude *benzole*; and in mustard oil. First prepared, in 1796, by Lampadius, by heating iron sulphide with charcoal. Composition was long uncertain. Clement a. Desormes (*A. Ch.* 42, 121) regarded it as a compound of C and S; it was also thought to be a compound of S and H, and at other times of C, S, H, and N. Composition established by Vauquelin, Berzelius, and Marcet, in 1812 (v. *G. A.* 28, 427 a. 453; 48, 177; *S.* 9, 284; *A. Ch.* 83, 252).

Formation.—1. By heating S with excess of C in a porcelain tube, condensing product in vessel surrounded by cold water, shaking with NaOHAq, drying by $CaCl_2$, and distilling from water bath.—2. By heating C with a metallic sulphide which gives off S at a high temperature, *e.g.* CuS or Sb_2S_3.—3. By heating wax, sugar, resin, &c., with S.—4. By heating $(CN)_2S$.—5. By heating CCl_4 with P_2S_5 to 200° in a closed tube.

Preparation.—Commercial CS_2 is distilled off quicklime at 60°–70°, leaving a little undistilled; the distillate is shaken in contact with powdered $K_2Mn_2O_8$, about 5 grams to 1 litre CS_2, for some time (to remove H_2S); it is then decanted and shaken thoroughly with Hg until fresh Hg is not blackened (various S compounds are thus removed); the liquid is poured off and again shaken with $HgSO_4Aq$ (abt. 25 g. salt per litre) until a few drops leave no trace of badly smelling residue when allowed to evaporate on filter paper; the CS_2 is poured off, allowed to stand in contact with $CaCl_2$, and then distilled (from a water bath) directly into the bottle in which it is to be preserved. It is kept in perfect dark

ness (Obach, *J. pr.* [2] 26, 281; for other methods *v.* Sidot, *C. R.* 69, 1303; Friedburg, *B.* 8, 1616; 9, 127; Millon, *J.* 1868. 928; Cloëz, *C. R.* 69, 1356).

Properties.—Colourless, limpid, highly refractive, liquid; ethereal odour when quite pure; vapour even when much diluted is poisonous, it stops fermentation (*v.* Cloëz, *C. R.* 63, 185). According to Wartha (*B.* 3, 80; 4, 180) CS_2 may be solidified by placing a *small quantity* in the vessel of a Carré freezing machine, exhausting the air, and then opening the stopcock while continuing to exhaust; in large quantities solid CS_2 is obtained by mixing with absolute ether and exhausting the air by a Carré machine. Wartha also obtained a snow-like solid by blowing dry air through CS_2 at the ordinary temperature; according to Ballo (*B.* 4, 118) this body is a hydrate of CS_2; Berthelot (*A. Ch.* [3] 46, 490) and Duclaux (*C. R.* 64, 1099) obtained such a hydrate (probably $2CS_2.H_2O$) by evaporating CS_2 in moist air (*v.* also Venables, *Am.* 5, 15). CS_2 vapour is very easily inflammable, ignition-temp. = 149° (Frankland, *C. N.* 6, 3), 170° (Braun); with air or O it forms a very explosive mixture; mixed with NO and ignited it burns instantaneously with production of white light rich in actinic rays (*v.* Berthelot, *A. Ch.* [3] 49, 486; Berzelius a. Marcet, *S.* 9, 284; Frankland, *C. N.* 6, 3; Sell, *B.* 5, 733; Delachanal a. Mermet, *D. P. J.* 214, 483). Water dissolves about $\frac{1}{1000}$ of its weight of CS_2 (Sestini, *G.* 1871. 473); it is miscible in all proportions with alcohol, ether, ethereal and fatty oils, and liquid CO_2 (*v.* Tuchschmidt a. Follenius, *B.* 4, 583). CS_2 is a solvent for fats, resins, gutta percha, alkaloids, I, S, P, &c. (*v.* Liebermann. *B.* 12, 1294; Gore, *P. M.* [4] 30, 414). According to Sidot, CS_2 is slowly changed in sunlight to CS and S (*v. ante*, CARBON MONOSULPHIDE).

Reactions.—1. *Heated*, strongly CS_2 gives C and S (Berthelot, *Bl.* [2] 11, 450; Buff a. Hofmann, *A.* 113, 129).—2. *Burns* in air or O to CO_2 and SO_2.—3. Decomposed by many *metals*; Fe is said to give CS at ord. temp. (Kern, *C. N.* 33, 253; *v.* also Merz a. Weith, *Z.* 11, 515); Cu at 200°–250° forms Cu_2S, S, and C (M. a. W.); K gives a sulphide and C; Na at 140°–150° forms Na_2S and Na_2CS_3, the latter body reacts with dilute HClAq to produce H_2CS_3 (Löw, *Z.* 9, 173; 10, 120); Na amalgam according to Löw (*l.c.*) gives C_2S_3, according to Raab (*N. R. P.* 19, 449) C_3S_2 (*v.* also Hermann, *J. pr.* 79, 448; Reichl, *C. C.* 1880. 420; Guignet, *Bl.* 1861. 111).—4. *Hydrogen*, when passed with CS_2 over heated Pt black, produces H_2S and C; nascent H (Zn and HClAq) forms H_2S and (?) $C_2H_4S_2$ (*v.* Vernon Harcourt, *C. N.* 26, 267; Cossa, *B.* 1, 117; Girard, *C. R.* 43, 396; Becquerel, *C. R.* 56, 237).—5. *Chlorine* reacts with CS_2 differently according to the conditions: dry Cl at ord. temp. gives S_2Cl_2 and CCl_4; moist Cl, or MnO_2 and HClAq, or other Cl producer, forms H_2SO_4 and $CSCl_2$ (Kolbe, *A.* 45, 41); Cl and CS_2 passed through a hot tube give S_2Cl_2 and CCl_4 (K.); Cl passed into boiling CS_2 containing a little I forms S_2Cl_2, CCl_4, and $CSCl_2$ (Müller, *C. J.* 15, 41); the same products result by action of ICl_3 (*v.* Weber, *W. A. B.* 1866. 348; Hannay, *C. N.* 37, 224).—6. *Chlorides which readily give up chlorine* react similarly to Cl: $MoCl_5$ and $SbCl_5$ give CCl_4 and S_2Cl_2, $SbCl_5$ also producing $SbCl_3S$ which separates into $SbCl_3$ and S (Aronheim, *B.* 9, 1788; Hofmann, *A.* 115, 264; Husemann, *A.* 117, 229); PCl_5 forms $CSCl_2$ (Carius, *A.* 113, 193), or according to Rathke (*Z.* 13, 57) CCl_4 and $PSCl_3$ (at 100°).—7. *Bromine* reacts in presence of I or $SbBr_3$; 2 parts CS_2, 14 parts Br, and 3 parts I, heated to 150° in a closed tube form CBr_4 (Bolas a. Groves, *B.* 3, 508; *v* also Berthelot, *A. Ch.* [3] 53, 145). Hell a. Urech describe a compound $C_2S_3Br_8$ obtained by slow action of Br and CS_2 and subsequent distillation (*B.* 15, 273).—8. *Water*, in presence of air, oxidises CS_2 slowly and partially to CO_2Aq and SO_3Aq (Berzelius); heated to 150° in a closed tube from 3 to 4 hours, CO_2Aq and H_2SAq are formed (Schlagdenhauffen, *J. Ph.* [3] 29, 401); evaporated in *moist air* a hydrate (?$2CS_2.H_2O$) is said to be formed (*v. Properties*). 9. Warmed with *sulphuric anhydride*, COS, SO_2, and S, are produced (Armstrong, *B.* 2, 712). 10. Mixed with *carbon dioxide* and passed through a hot tube, or over hot Pt black, COS is produced (Winkler).—11. Passed through a hot tube with *sulphuric acid*, CO, SO_2, H_2S, and S are formed (W.).—12. Many *metallic oxides* when heated with CS_2 react to form sulphides, sometimes also carbonates (Schlagdenhauffen, *J. Ph.* [3] 29, 401; Müller, *P.* 127, 404; Fremy, *C. R.* 35, 27).—13. *Oxidising agents, e.g.* KNO_3 or $K_2Mn_2O_8$, generally produce CO_2 and H_2SO_4, sometimes CO_2 and H_2S; As_2O_3, As_2O_5, (and salts of these) produce As_2S_3 (*v.* Schlagdenhauffen, *l.c.*; Cloëz a. Guignet, *C. R.* 46, 1110). 14. *Boric acid and borates* react at red heat to form B_2S_3.—15. *Sulphuretted hydrogen* mixed with CS_2 and passed over hot Cu produces CH_4. 16. *Alkalis in aqueous solution* form carbonates and thiocarbonates (*v.* THIOCARBONATES, under CARBONIC ACID, &c.); *alcoholic potash* forms K xanthate $C_2H_5O.CS.SK$. — 17. *Ammonia* reacts with CS_2 probably to form $CS(NH_2)_2$ and $(NH_4)_2CS_3$ (Laurent, *A. Ch.* [3] 22, 103; Zouteveen, *C. C.* 1870. 821); CS_2 and NH_3 passed through a hot tube, or CS_2 heated in a closed tube with alcoholic NH_3, produce H_2S and HCNS; alcoholic NH_3 at ord. temp. forms $(NH_4)_2CS_3$, $(NH_4)CNS$, and $CS.NH_2.SNH_4$ (Debus, *A.* 73, 26; *v.* also Millon, *J. Ph.* [3] 38, 401; Hofmann, *J.* 1858. 332); NH_3Aq form $(NH_4)_2CS_3$Aq and NH_4.CNSAq.

Combinations.—1. With many *metallic sulphides* to form *thiocarbonates* (*q. v.*).—2. With various *ammonia derivatives*; *e.g.* $NMe_3.CS_2$. 3. With *zinc ethyl and methyl* to form $ZnEt_2.CS_2$, and $ZnMe_2.CS_2$, respectively.—4. With *triethylphosphine* to form $PEt_3.CS_2$.

Analysis.—Sulphur, by heating in a glass tube with Na_2CO_3 and a little KNO_3, and estimating sulphates produced, as $BaSO_4$. Carbon, by burning with $PbCrO_4$ as in organic analyses.

Detection and Estimation.—Small quantities of CS_2 may be detected by adding alcoholic solution of potash, whereby K xanthate ($C_2H_5O.CS.SK$) is formed; on now adding solution of a copper salt a yellow pp. is produced (Vogel, *A.* 86, 369). This reaction is applied to liquids, *e.g.* mustard oil, by distilling a little in a current of air into alcoholic potash; coal-gas may be tested by passing through

alcoholic potash. A very delicate reaction is to bring the CS_2 into contact with PEt_3 when a characteristic carmine-red compound, $PEt_3.CS_2$, forms; it may be crystallised from ether. This reaction may also be applied for the estimation of CS_2 (Hofmann, *B.* 13, 1732). CS_2 is sometimes determined, *e.g.* in xanthates, by standardised $CuSO_4Aq$ (Grete, *B.* 9, 921); thiocarbonates may be converted into the Pb salt (by addition of Pb acetate), and this may be decomposed by boiling with water, and the CS_2 led into weighed bulbs containing alcoholic potash (Delachanal a. Mermet, *B.* 8, 1192).

Carbon, sulphochlorides of.

I. THIO-CARBONYL CHLORIDE. $CSCl_2$. Mol. w. 114·69. (70°). V.D 57·5.

Formation.—1. By reaction between Cl and CS_2.—2. By heating CCl_4 with S.—3. By passing CCl_4 and H_2S through a hot tube (Kolbe, *A.* 45, 41; Carius, *A.* 113, 193; Müller, *C. J.* 15, 41; Gustavson, *B.* 3, 989).

Preparation.—To dry CS_2 about ·2 p.c. I is added and dry Cl is passed in (a reversed condenser being attached) until the volume of liquid has increased by about $\frac{1}{3}$. The whole is boiled with water (to remove S_2Cl_2); separated S is removed, water is separated, the liquid is distilled from the water-bath whereby CCl_4 and CS_2 distil over; the residue is then distilled till a thermometer in the liquid reaches 175°; the distillate is fractionated, digested with water to remove S_2Cl_2, dried, and fractionated. About 320 g. $CSCl_4$ (*v. infra*) are thus obtained from 1 kilo. CS_2; very finely divided silver (by reducing AgCl) is then added little by little (the liquid being kept cold) until the whole of the liquid is soaked into the silver; it is then distilled, the distillate is shaken with water to remove traces of S_2Cl_2, dried, and fractionated (Rathke, *B.* 3, 858). The reactions are (1) $2CS_2 + 5Cl_2 = 2CSCl_4 + S_2Cl_2$; (2) $CSCl_4 + 2Ag = 2AgCl + CSCl_2$.

Properties and Reactions.—Golden-red, limpid, liquid; penetrating odour, resembling that of $COCl_2$; fumes in air. Exposed to light and then to a low temperature, large colourless crystals of a polymeride, $nCSCl_2$, separate; this body is unchanged in air; melts at 112·5°; is volatilised in steam; at 180° in a closed tube it gives $CSCl_2$.

II. THIONYL PERCHLORIDE. $CSCl_4$ (Rathke, *B.* 3, 858). Prepared by action of Cl on CS_2 (*v.* THIONYL CHLORIDE, *Preparation*). A clear, golden-yellow liquid; vapour causes free flow of tears; B.P. 146°–147°; S.G. 1·712 at 12·8°. Decomposed, slowly by moist air, quickly by heating with water to 160°, to CO_2, HClAq, and S. Heated to 200° is decomposed to CCl_4, S_2Cl_2, and a little $CSCl_2$. M. M. P. M.

CARBONATES *v.* CARBONIC ACID, CARBONATES, and THIO-CARBONATES.

CARBON TETRA-BROMIDE *v.* TETRA-BROMO-METHANE.

DI-CARBON-TETRA-CARBOXYLIC ACID *v.* ETHYLENE-TETRA-CARBOXYLIC ACID.

CARBONIC ACID, CARBONATES, AND THIO-CARBONATES.

CARBONIC ACID. A solution of CO_2 in water probably contains carbonic acid, H_2CO_3. The chief reasons for this statement are as follows. The mass of CO_2 dissolved by water at ordinary temperatures and small pressures (less than 760 mm.) varies as the pressure. But at pressures of 2, 3, or more atmospheres, the mass of CO_2 dissolved is less than that calculated by the law of Henry a. Dalton. Khanikoff a. Longuinine (*A. Ch.* [4] 11, 412) give these numbers:—P = pressure in mm., a = vol. of CO_2 (measured at 0° and 760 mm.) dissolved by 1 vol. water at about 15°.

P.	a.	P.	a.
697·71	0·9441	2188·65	3·1764
809·03	1·1619	2369·02	3·4857
1289·41	1·8647	2554·0	3·7152
1469·95	2·1623	2738·33	4·0031
2002·06	2·9076	3109·51	4·5006

When the pressure is decreased to 760 mm. over water saturated with CO_2 at pressures greater than 760 mm. most of the CO_2 escapes, at first rapidly, then slowly; the last traces of CO_2 can be removed by placing the water *in vacuo*, or by long-continued boiling. Magnesium reacts with a solution in water of CO_2 to form $MgCO_3$ and H; the quantity of H evolved is almost exactly that calculated on the hypothesis that the reaction is $H_2CO_3Aq + Mg = MgCO_3 + H_2$ (Ballo, *B.* 15, 3003). Water holding in solution Na_2CO_3 or K_2CO_3 dissolves considerably more CO_2 than pure water; $NaHCO_3$ (or $KHCO_3$) is produced (Ballo, *l.c.*). Mg reacts with aqueous solutions of $NaHCO_3$ or $KHCO_3$ to form $MgCO_3$, K_2 (or Na_2)CO_3, and H (Ballo, *l.c.*). Aqueous solution of CO_2 turns blue litmus wine-red, the blue colour returns on exposure to air; blue litmus in contact with CO_2 at pressures of $1\frac{1}{2}$ to 2 atmospheres becomes vermilion-red (Malaguti, *A. Ch.* [3] 37. 206). When CO_2 dissolves in water, heat is produced; $[CO^2,Aq] = 5,880$ (*Th.* 1, 260). This solution reacts thermally with alkalis as a dibasic acid; thus (Thomsen)—

n	$[CO^2Aq, nNaOHAq]$
1	11,016
2	20,084

The thermal value of the second formula-weight of NaOH (9,068) is considerably less than that of the first (11,016); in this respect carbonic acid behaves like sulphurous, selenious, boric, acid, &c. (*v.* ACIDS, BASICITY OF). When moist CO_2 reacts with KOH, K_2CO_3 is obtained; from this a great many carbonates may be formed, the composition of which is that of metallic derivatives of a dibasic acid H_2CO_3. The aqueous solutions of carbonates are decomposed by almost all acids, not by HCNAq or $H_2B_4O_7Aq$; hence the *affinity* of carbonic acid is small (*v.* AFFINITY). But soluble silicates are at once decomposed by CO_2Aq, and even insoluble silicates *e.g.* of Ca, Al, &c. are slowly decomposed by moist CO_2. The sulphur analogue of carbonic acid – H_2CS_3 – has been isolated. Finally various derivatives, both of $CO(OH)_2$ and $CS(SH)_2$ are known; viz. $COCl_2$, (?$COBr_2$), $CO(NH_2)_2$, COS, $CSCl_2$, $CS.NH_2.SH$, $CS(NH_2)_2$.

CARBONATES. *Normal carbonates* have the composition M_2CO_3 or MCO_3. Certain *acid carbonates*, $MHCO_3$, have also been isolated; very few of these are known as definite solids, the principal are when M = Na, K, NH_4 (?Tl). Some insoluble normal carbonates, *e.g.* Ba, Mg, Fe, dissolve in water saturated with CO_2; at a

pressure of 4 or 5 atmos. acid carbonates are probably formed. Many *'basic' carbonates* exist; these are most simply represented by the general formula $xMO(or M_2O_3).yCO_2.zH_2O$. A few *double carbonates* are also known, usually compounds of alkali carbonates with others, *e.g.* $(NH_4)_2CO_3.MgCO_3$; $K_2CO_3.NiCO_3.4H_2O$. Several ethereal carbonates are known, derived from the hypothetical *ortho-carbonic acid* $C(OH)_4$; *e.g.* $C(OEt)_4$, $C(OPr)_4$ (*v.* CARBONIC ETHERS).

Formation.—1. By reaction between metallic oxides or hydroxides and CO_2 in presence of water; the oxides which act as weak bases, Fe_2O_3, Al_2O_3, &c., do not combine with CO_2 when dry.—2. By pp. from solutions of salts by alkali carbonate solutions; only the salts of BaO, SrO, CaO, Ag_2O, and HgO, yield normal carbonates; other salts give basic carbonates containing less CO_2, relatively to MO, the weaker is the oxide MO, and the warmer and more dilute is the solution; salts of such weak bases as Fe_2O_3, Al_2O_3, and SnO, give pps. of hydrates free from CO_2.—3. By strongly heating the alkali or alkaline earth salts of organic acids.—4. In some cases by reaction between CO_2Aq and a metal; *e.g.* Mg, Fe, Zn.

Solubility in water.—Carbonates of Na, K, Rb, and Cs, are easily soluble in water; carbonates of Li and Tl are much less soluble; other carbonates are nearly, or quite, insoluble. All carbonates are soluble, to some extent, in water in which CO_2 has been dissolved. All, except those of NH_4, Rb, and Cs, are insoluble in alcohol.

Reactions.—1. All carbonates, except those of the fixed alkalis, are wholly or partially decomposed by *heat* alone; $BaCO_3$ begins to decompose only at a full white heat, $SrCO_3$ at beginning white heat, and $CaCO_3$ at full red heat; Ag_2CO_3 gives up CO_2 at 200°, and at 250° the Ag_2O gives off O and leaves Ag; $MnCO_3$ heated to 200°-300° in air gives MnO_2 and CO_2.—2. *Heated in steam* all carbonates are decomposed to hydrates and CO_2 (*v.* Rose, *P.* 85, 99 a. 279).—3. Carbonates are decomposed by aqueous solutions of most *acids* at ordinary temperatures with evolution of CO_2; HCNAq and $H_2B_2O_4$Aq, however, do not decompose carbonates.—4. Solid carbonates are decomposed by heating with solid *boric acid, silica, potassium dichromate*, and some other salts. *Sulphuretted hydrogen* reacts with many insoluble carbonates suspended in water, *e.g.* of Sr, Ba, Ca, Zn, Mg, Li, to form sulphides and CO_2; the change proceeds the further the more water is present (Naudin a. Montholon, *C. R.* 83, 58).—5. The more stable carbonates when *heated with carbon* give CO.—6. Alkali carbonates *heated in phosphorus - vapour* give phosphates and C.—7. Aqueous solutions of acid carbonates do not usually affect the colour of *litmus*; they give an alkaline reaction with *rosolic acid*.

Detection and Estimation.—Usually detected by decomposing by an acid and examining action of gas evolved on CaO$_2$H$_2$Aq. Usually estimated by decomposing weighed quantity by acid and determining CO_2 by loss.

Aluminium carbonate. Existence doubtful. Pp. produced by alkaline carbonates with Al salts variously formulated as a highly hydrated basic carbonate (Muspratt, *C. J.* 2, 206; Langlois, *A. Ch.* [3] 48, 502; Wallace, *C. Gazette*, 1858. 410); as a compound of $Al_2O_6H_6$ and a small quantity of the carbonate employed, *e.g.* $Al_2(HO)_6 + 2NH_4HCO_3$ (Rose, *P.* 41, 462); and as pure $Al_2O_6H_6$ (Barratt, *C. J.* 13, 190). By Wibain and Renoul the pp. in the cold is said to be $2Al_2O_3.CO_2.8H_2O$ and to decompose about 30° (*C. R.* 88, 1133) (*v.* also H. Rose, *P.* 91, 460; Parkmann, *Am. S.* [2] 34, 324).

Ammonium carbonates. Three definite salts seem to exist, the normal, the acid, and the sesqui, carbonate (Divers, *C. J.* [2] 8, 171). The last is sometimes regarded as a compound of the first and second (Deville, *C. R.* 34, 880). Divers considers the compositions of the three salts to be:

Normal carbonate, $2CO_2.4NH_3.4H_2O$.
Sesquicarbonate, $3CO_2.4NH_3.4H_2O$.
Acid carbonate, $4CO_2.4NH_3.4H_2O$.

Rose's *hyperacid carbonate* may be the fourth term of this series.

I. *Normal carbonate* $(NH_4)_2CO_3.H_2O$. Prepared (1) by adding excess of NH_3Aq to a warm conc. solution of the commercial carbonate; (2) by warming water with the ordinary carbonate, and allowing solution to cool and crystallise; after this has been done repeatedly the cold mother liquor from the last crop of crystals deposits normal carbonate. Large elongated plates, freely soluble in water, insol. alcohol, sparingly sol. NH_3Aq. Decomposes in air to NH_4HCO_3, with evolution of NH_3, and at 85° to NH_3, CO_2, and H_2O. Is converted into carbamate by digestion in closed vessel at 20°-25°.

II. *Acid carbonate* NH_4HCO_3. Occurs in guano-deposits (Ulex, *A.* 61, 44). Prepared by saturating NH_3Aq, or solution of NH_4 sesquicarbonate, with CO_2, and drying over H_2SO_4 and KOH. S. (0°) 11·9; (10°) 15·85; (20°) 21; (30°) 27 (Dibbits, *J. pr.* [2] 10, 417). This is the stable salt to which the other NH_4 carbonates are converted. Large, transparent, trimetric crystals. Dimorphous, but never isomorphous with $KHCO_3$ (Deville). Solution at 36° evolves CO_2; even at ordinary temperature unstable in solution.

III. *Sesquicarbonate.* $(NH_4)_2CO_3.2NH_4HCO_3$. By slowly heating the commercial salt till melted and then cooling; or crystallises from warm solution of the same salt mixed with NH_3Aq. Large transparent crystals, losing H_2O and NH_3 in air and giving NH_4HCO_3. S. (13°) 25; (17°) 30; (32°) 37; (41°) 40; (49°) 50 (Berzelius). Solution easily decomposes with evolution of CO_2.

Another carbonate—$(NH_4)_4CO_4$—appears to exist in the mother-liquor from the preparation of the sesquicarbonate (Divers). The *commercial carbonate* is probably $3NH_3.2CO_2.H_2O$. It generally contains 1 p.c. H_2O in excess of this formula, and a little ammonia. Prepared (1) by dry distillation of animal matter and subsequent purification by redistillation with charcoal; (2) by heating to redness NH_4Cl and $CaCO_3$ in retort with receiver. The first products are H_2O and NH_4 carbamate, subsequent distillation produces the commercial carbonate. A white, transparent, fibrous mass, with strong ammoniacal smell, volatile, but not without some decomposition. Solution strongly alkaline.

Barium carbonate. $BaCO_3$. By adding $(NH_4)_2CO_3Aq$ to $BaCl_2Aq$ or $Ba(NO_3)_2Aq$; or Na_2CO_3Aq to $BaSAq$; or (impure) by strongly heating a mixture of $BaSO_4$, charcoal, and K_2CO_3, and extracting the K_2S formed with water, leaving $BaCO_3$. S. = 0; in water saturated with CO_2 at 4 to 6 atmos. pressure S = ·75. The salt remains in solution at ordinary pressure, but is completely ppd. on boiling (Wagner, *J. pr.* 102, 233; *J.* 1867. 135). Found native as *Witherite*. This mineral can be obtained artificially from amorphous $BaCO_3$ by crystallising from fused KCl and NaCl (Bourgeois, *Bl.* [2] 37, 447). A soft white poisonous powder, easily soluble in solution of NH_4Cl, NH_4NO_3, or ammonium succinate. Above red heat in presence of C it yields BaO and CO_2. Decomposed at red heat by aqueous vapour especially in presence of chalk. Yields $BaSO_4$ when shaken with K_2SO_4 or Na_2SO_4Aq, and is completely decomposed by boiling with NH_4ClAq.

Barium acid carbonate, $2BaCO_3.CO_2$, described by Boussingault (*A. Ch.* [2] 29, 280) but Rose thinks it cannot exist except in solution.

Beryllium carbonate. A compound of variable composition is obtained by exposing $Be(HO)_2$ to air, ppg. beryllium salts with alkaline carbonates, or boiling solution of double $Be\text{-}NH_4$ carbonate. The composition of pp. by last method is $5BeO.CO_2.5H_2O$ (Schaffgotsch). Decomposed by boiling water, soluble in alkaline carbonates. The salt $BeCO_3.4H_2O$ is obtained by passing CO_2 through water containing basic salt in suspension and evaporating over H_2SO_4 in atmosphere of CO_2.

Beryllium ammonium carbonate. $2(BeCO_3.(NH_4)_2CO_3).Be(HO)_2.2H_2O$. By dissolving BeO in conc. Am_2CO_3Aq at gentle heat, then boiling till solution becomes cloudy, filtering, and adding conc. alcohol; crystals are drained, washed with alcohol, and dried by pressing between paper (Humpidge, *Pr.* 39, 14). By similar method Deville (*A. Ch.* [3] 44, 5) obtained a salt of formula $3(BeCO_3.(NH_4)_2CO_3).Be(HO)_2$ soluble in cold, and decomposed by hot, water.

Bismuth carbonate. $Bi_2O_3.CO_2$ (Berzelius) a white pp. obtained by dropping a solution of $Bi3NO_3$ into an alkaline carbonate. According to Lefort this pp. contains ½ H_2O evolved at 100°. Heated strongly yields $Bi_2O_3.3(BiO)_2CO_3.2BiO_3H_3.3H_2O$. Occurs native as *Bismuthite* in South Carolina.

Cadmium carbonate. $CdCO_3$(?) Occurs native with $ZnCO_3$. By ppg. solution of a cadmium salt with $(NH_4)_2CO_3Aq$. The white pp. is said to contain water, which is lost at 80°–120°, and at a higher temp. to lose CO_2 and leave CdO (Lefort, *J. Ph.* [3] 12, 78); Rose (*P.* 85, 304) says pp. is nearly represented by $CdCO_3$. Moist $Cd(HO)_2$ absorbs CO_2 and at 300° loses all its water, leaving $2CdO.CdCO_3$.

Cæsium carbonate Cs_2CO_3. S. alcohol (19°) = 11·1. Ill-defined hydrated deliquescent crystals separate from a syrupy solution. On melting these leave Cs_2CO_3 as sandy powder. *Acid carbonate*, $Cs.H.CO_3$, crystallises from aqueous solutions in large prisms.

Calcium carbonate. $CaCO_3$. S. (cold) = ·0094; (100°) = 1·13 (Fresenius, *A.* 59, 117); S. (0° in water saturated with CO_2) = ·07, (10°) = ·088 (Lassaigne, *J. Chem. Med.* 1848. 312; Schlœsing, *C. J.* [2] 10, 788).

Occurrence.—Native; in rhombohedra (hexagonal) as *calcspar*, S.G. 2·69–2·75; and in right rhombic prisms (trimetric), S.G. 2·92–3·28, as *arragonite*; also abundantly as chalk, limestone, &c. Formed when hydrated or anhydrous CaO is exposed to moist air; but not by action of CO_2 on dry CaO.

Preparation. — 1. By ppg. $CaCl_2Aq$ by $(NH_4)_2CO_3Aq$. From not too dilute solutions below 30°, it is ppd. entirely as calcspar; above 30° the pp. contains arragonite, in gradually increasing quantity as the temp. rises, until about 90° the pp. is almost entirely arragonite. $CaCO_3$ which separates as calcspar from a cold, not too dilute, solution of the acid carbonate, is deposited partly in arragonitic form on addition of a very little $PbCO_3$, $CaSO_4$, or $SrSO_4$ (Credner, *J. f. Mineral.* 1871. 288). The arragonite tends to change to calcspar form if left under cold solution. Can be obtained in form of calcite from ppd. carbonate by crystallising from fused NaCl and KCl (Bourgeois, *Bl.* [2] 37, 447).

Properties and Reactions.—Tasteless, white, slightly alkaline; easily soluble, when recently ppd., and to a certain extent even when it becomes crystalline, in aqueous solutions of $(NH_4)_2CO_3$, NH_4Cl, NH_4NO_3, and ammonium succinate. These salts, therefore, prevent complete ppn. of calcium as carbonate. At full *red heat* is decomposed into CO_2 and CaO. Temp. of decomposition is lowered by passing air or steam over the $CaCO_3$. In closed tube fuses to marble-like substance. *Boiling ammonium chloride* solution decomposes $CaCO_3$ forming $CaCl_2$ and $(NH_4)_2CO_3$. *Sulphur* decomposes $CaCO_3$ forming $CaSO_4$ without previous formation of H_2S (Podacci, *G.* 1874. 177). The sulphur is oxidised at expense of oxygen of water (Brugnatelli a. Pelloggio, *G.* 1874. 536), and the formation of sulphuric acid is preceded by that of penta- and tetra-thionic acids (Bellucci, *S.* 1874. 179). A salt of the formula $CaCl_2.2CaCO_3.6H_2O$ was obtained by Pelouze (*Bl.* [2] 3, 183).

Hydrates: above 30° $CaCO_3$ is ppd.; below 30° hydrates are formed containing amounts of water (10–27 p.c.) which vary with the temp. and time occupied in ppn. From a solution of lime in sugar-water cooled to 0°–2°, a hydrate $CaCO_3.6H_2O$, decomposed at 30°, is obtained; while the same solution at a little higher temp. yields $CaCO_3.5H_2O$ crystallising in rhombohedra, S.G. 1·783, decomposed above 15° even in water (Pelouze, *Bl.* [2] 5, 183). Same hydrate found by Scheerer (*P.* 68, 382) and Rammelsberg (*B.* 4, 469). A gelatinous hydrate formed by action of CO_2 on CaO and water is described by Bondonneau (*Bl.* [2] 23, 100).

Acid carbonate $CaH_2(CO_3)_2$ (?) is known only in solution; obtained by passing CO_2 into cold water containing suspended $CaCO_3$. Decomposed with separation of $CaCO_3$ on exposure to air, or more quickly on boiling.

Basic carbonate $2CaO.CO_2$. Obtained from $CaCO_3$ at a moderate red heat. Hardens by action of water, forming $CaCO_3.CaO_2H_2$, which is also produced by exposing CaO to moist air. This hydrate gives $2CaO.CO_2$ at low

red heat, and at strong red heat gives off CO_2 and H_2O (Fuchs, *P.* 27, 601).

Cerium carbonate $Ce_2(CO_3)_3.9H_2O$ by exposing Ce_2O_3 to air or by ppn. A white powder, partially converted on heating strongly in air into Ce_2O_3.

Chromous carbonate $CrCO_3$. An amorphous greyish-white substance, prepared by heating a chromous salt with Na_2CO_3Aq out of contact with the air (Moissan, *A. Ch.* [5] 25, 401).

Cobalt carbonate $CoCO_3$. By heating $CoCl_2$ with $CaCO_3$ to 150° in sealed tube for 18 hrs., or by decomposing $CoCl_2$ with a solution of $NaHCO_3$ supersaturated with CO_2 and heated to 140° in a strong vessel allowing slow escape of CO_2. Light, rose-coloured, sandy powder; microscopic rhombohedra; not attacked by acids in the cold (Senarmont, *A. Ch.* [3] 30, 129).

Hydrated carbonates and *double salts* are formed on adding cobalt solutions to alkaline carbonates. Hot or cold, not too dilute, solutions yield a rose-coloured pp., which dried at 100° is $2CoCO_3.3Co(HO)_2$ (Setterberg, *P.* 19, 55; Winkelblech, *A.* 13, 148; Rose, *ibid.* 80, 237). Boiling water partially converts it into Co_2O_3 (Field, *C. J.* 14, 50); digested with $NaHCO_3$ or $(NH_4)HCO_3Aq$ yields $3CoCO_3.H_2O$ (Deville, *A. Ch.* [3] 33, 75). Hot very dilute solutions yield blue $CoCO_3.2Co(HO)_2aq$. Heated above 150° both pps. give off H_2O and CO_2, yielding Co_2O_3 (Rose).

Cobalt-potassium carbonate $(CoKH)(CO_3)_2.4H_2O$. Rose-coloured crystals, prepared by action of excess of $KHCO_3Aq$ on $Co(NO_3)_2$ or $CoSO_4Aq$. Decomposed by water (Rose; Deville). Deville also obtained $CoK_2(CO_3)_2.4H_2O$.

Cobalt-sodium carbonate $CoNa_2(CO_3)_2.4H_2O$. Prismatic, and $CoNa_2(CO_3)_2.10H_2O$ dark red, crystals; obtained together by the action of $Co2NO_3Aq$ on solution of Na sesquicarbonate (Deville).

Copper carbonate. Unknown except in solution. Obtained by dissolving the ppd. basic carbonate in CO_2Aq at 4–6 atmospheres pressure (Wagner, *J. pr.* 102, 233).

Hydrated basic carbonates.

$CuCO_3.CuO_2H_2$ occurs native as *malachite*. Prepared by ppg. a cupric salt with an alkaline carbonate. The pp. at first is greenish blue, and is said to contain 1 mol. H_2O; left in contact with liquid and washed it has above composition and is dark green. Heated to 200° yields malachite. Boiled with water it yields CO_2 and CuO (H. Rose; Field, *C. J.* 14, 71). Digested with $(NH_4)_2CO_3Aq$ at 48·8° it is converted into $CuCO_3.5CuO$, a dense black powder, which is also obtained by prolonged boiling $CuSO_4Aq$ with $Am_4H_2(CO_3)_3$, filtering from $CuCO_3.Cu(HO)_2$, and adding more $CuSO_4$ (Field). Digested with Na_2CO_3 yields $CuCO_3.7CuO.5H_2O$.

The basic salt $2CuCO_3.Cu(HO)_2$ occurs native as *asurite* in blue monoclinic crystals. Boiled with water yields CuO and evolves CO_2. With hot $NaHCO_3$ yields a blue solution which after protracted boiling, deposits $CuCO_3.CuO_2H_2$ (Field). Prepared artificially by secret process (Phillips, *A. Ch.* [2] 7, 44). *Asurite* can be formed from malachite at ordinary temps. by addition of CO_2 and abstraction of H_2O in presence of a dehydrating agent and CO_2 at high temp. (Weibel, *J. für Mineral.* 1873. 245). Crystallised $Cu(NO_3)_2$ heated with $CuCO_3$ under a pressure of 54 atmospheres yields crystalline warty mass of asurite (Debray).

Double salts. *Potassic-cupric carbonate* $5CuO.K_2O.CO_2.10H_2O$. A dark-blue silky mass, obtained by adding $Cu(NO_3)_2$ to $KHCO_3$.

Sodic-cupric carbonate $CuNa_2(CO_3)_2.6H_2O$. By action of $NaHCO_3$ on $CuCO_3.CuO_2H_2$ at 40°–50°. Rhombic prisms.

Cuprammonium carbonate $(NH_3)_2Cu.CO_3$. Obtained as dark-blue crystals by dissolving basic carbonate of copper in Am_2CO_3 and pouring solution into alcohol. Water decomposes it into Am_2CO_3 and $CuCO_3.CuO.Cu(HO)_2$ (Favre, *Traité de Chem.* par Pelouze et Frémy). Also formed when CuO or Cu is digested in NH_3Aq with access of air.

Didymium carbonate. $Di_2(CO_3)_3$. A red crystalline powder obtained by passing CO_2 into water containing suspended DiO_3H_3. A hydrated carbonate is obtained, as a very slightly rose-coloured pp., by adding an alkaline carbonate to solution of a Di salt. Loses $\frac{2}{3}$ H_2O and a little CO_2 at 100° (Marignac).

Indium carbonate. In_23CO_3. White, gelatinous pp., soluble in $(NH_4)_2CO_3Aq$, and ppd. on boiling; insoluble in solution of fixed alkali carbonates (Winkler, *J. pr.* 94, 1).

Iron carbonates. *Ferric carbonate* does not appear to exist (Gmelin; Soubeiran, *A. Ch.* [2] 44, 326). Double salts of *ferricum* and alkaline carbonates appear to exist in solution, as the pp. of ferric hydrate obtained by conc. alkaline carbonate solutions gradually redissolves, whereas pure well-washed $Fe_2O_6H_6$ does not dissolve in these solutions.

Ferrous carbonate, $FeCO_3$, occurs abundantly as *spathic ore*. Prepared by methods similar to those described for $CoCO_3$ (*q. v.*). It is a greyish-white crystalline solid, composed of minute rhombohedra; scarcely attacked by dilute acids, nearly unchanged in dry air. It is darker and less alterable the higher the temperature at which it has been formed, and the longer it has been heated (Senarmont, *A. Ch.* [3] 30, 129). Spathic ironstone dissolves under pressure in water saturated with CO_2 (S. = ·72), and is deposited as a black amorphous pp. on boiling (Wagner, *J.* 1867, 135).

Hydrated ferrous carbonate, $FeCO_3.H_2O$, occurs native. Amorphous, white, earthy, little altered in air, scarcely decomposed by acids at ordinary temps. (Moissan, *C. R.* 59, 238). The hydrate obtained by ppg. solution of a ferrous salt with an alkaline carbonate rapidly decomposes on exposure to air. It can be obtained fairly pure, as a greenish tasteless powder, by ppg. ferric-free ferrous sulphate with normal or acid alkaline carbonates. The salts are dissolved in de-aërated water, the pp. washed by decantation out of contact with air, and dried in CO_2. If dry it is fairly permanent; if moist it gives off H_2O and CO_2; but if mixed with sugar the change is less rapid.

Ferrous-hydrogen carbonate. Solution of CO_2 dissolves $FeCO_3$ and Fe; the latter with evolution of H.

Lanthanum carbonates. $La_2(CO_3)_3.8H_2O$. Found native as *Lanthanite* in four-sided plates or minute tables of the trimetric system.

The carbonate obtained by ppn. forms a white gelatinous mass which changes to shining crystalline scales. $2La_2(CO_3)_3.15H_2O$; ppd. by Na_2CO_3Aq from La_23SO_4Aq, and dried at ordinary temperature. Micaceous scales with silky lustre (Hermann, *J. pr.* 82, 385).

Lead carbonate. $PbCO_3$. Occurs native in trimetric crystals as *white lead ore* or *cerusite*. Has also been found on bronze objects from Pompeii (Luca, *C. R.* 84, 1457). Prepared by ppg. $Pb(NO_3)_2Aq$ with excess of alkaline carbonates in the cold (Berzelius; Lefort, *J. Ph.* [3] 15, 26). According to Rose (*A.* 80, 235) these pps. are all hydrocarbonates, the ratio of hydrate to carbonate increasing with the temp. and dilution of the solutions. Bodies of the same composition are formed by direct action of CO_2 on $Pb(HO)_2$, but differ in being amorphous and opaque, instead of consisting of minute transparent crystalline grains.

White lead is a hydrocarbonate presenting varieties of composition represented by (1) $2PbCO_3.PbO_2H_2$; (2) $5PbCO_3.3PbO_2H_2$; (3) $3PbCO_3.PbO_2H_2$ (Mulder, *A.* 33, 242); (4) $5PbCO_3.PbO_2H_2$ (Phillips, *C. J.* 4, 165). Prepared by (1) *Dutch method*. Thin lead sheets are placed over gallipots containing weak acetic acid ($2\frac{1}{2}$ p.c.); the pots are embedded in fermenting tan at a temp. of 60°–65°. The metal disappears in a few weeks. Oxide of lead is first formed, and dissolved by the acetic acid, forming a basic acetate, and this is decomposed by the CO_2 evolved from the tan. (2) PbO is mixed with water and about 1 p.c. of Pb acetate, and CO_2 is passed over it. $Pb(NO_3)_2$ has been used instead of acetate. Nearly insol. in sat. CO_2Aq even under pressure (Wagner). The ppd. carbonate has S. = ·05 in sat. CO_2Aq.

Lead-sodium carbonate. $4PbCO_3.Na_2CO_3$ (Berzelius, *P.* 47, 199).

Lead-chloro-carbonate. A compound of the chloride and carbonate of lead is obtained as a pp. by the action of CO_2 under pressure on $PbCl_2$ (Miller, *C. J.* [2] 8, 37).

Lithium carbonate. Li_2CO_3. S.(0°) = 1·539; (50°) = 1·181; (100°) = ·728 (Bevade, *Bl.* [2] 43, 123). Found in many mineral waters. Prepared by dissolving an excess of $(NH_4)_2CO_3$ in conc. LiClAq, and washing resulting pp. with alcohol, or by strongly heating Li acetate. Not decomposed by heat. Melts at low red heat, and solidifies to a vitreous mass on cooling. The solution is alkaline and decomposes NH_4 salts, but is decomposed by $Ba(HO)_2$ and $Ca(HO)_2$. By slow evaporation the solution deposits salt in small prisms. Water saturated with CO_2 dissolves it more readily than pure water.

Magnesium carbonate. $MgCO_3$. Occurs native as *magnesite*, in rhombohedral crystals isomorphous with calcspar; infusible; dissolves slowly in acids. *Prepared* (1) By suspending in water the washed pp. obtained by adding solution of an alkaline carbonate to solution of a Mg salt (which always contains MgO_2H_2), passing CO_2 through the liquid till pp. is dissolved, and evaporating by heat (Rose, *P.* 42, 366); (2) By heating $MgSO_4Aq$ with Na_2CO_3Aq to 160° in a sealed tube; (3) By inclosing a soluble Mg salt with an alkaline-hydrogen carbonate, saturated with CO_2, in a strong vessel closed by a cork through which the CO_2 can slowly escape (Senarmont, *C. R.* 28, 693); (4) By carefully heating $MgCO_3.KHCO_3.4aq$ to 200°, and extracting with water (Engel, *Bl.* [2] 44, 355). A white crystalline powder, isomorphous with arragonite by method (1); obtained in rhombohedra by (3); isodimorphous with $CaCO_3$. When moist it is alkaline to litmus. $CaSO_4Aq$ partially decomposes it, especially in presence of NaClAq (Fleischer, *J. pr.* [2] 6, 273). Soluble in cold solutions of alkaline borates, ppd. on heating, but redissolved on cooling (Wittstein, *Ar. Ph.* [3] 6, 40). *Hydrates* (α) $MgCO_3.3H_2O$. Hexagonal prisms obtained by spontaneous evaporation of a solution of $MgCO_3$ in excess of CO_2Aq. They lose water in dry air but retain their form. (β) $MgCO_3.5H_2O$. Transparent oblique prismatic crystals obtained by exposure of above solution at a low temp. Converted into (α) by exposure to air &c. Boiled, they yield $4MgCO_3.MgH_2O_2.4aq$ (Fritzsche; *v.* also Engel, *C.R.* 101, 814).

Hydrocarbonates. As in the case of lead, the composition of pp. formed by adding an alkaline carbonate to solution of a Mg salt depends on proportions, strength, and temp., of solutions. A variable mixture of hydrocarbonates is known as *magnesia alba*; (α) $4MgCO_3.MgH_2O_2.4aq$; a white granular powder (for preparation *v.* Rose, *A.* 80, 234). (β) $3MgCO_3.Mg(HO)_2.3aq$, occurs native as *hydromagnesite* in small white monoclinic crystals (Dana). Prepared artificially (Berzelius, Fritzsche) it is a white, slightly soluble powder forming alkaline solutions. Dried at 100° in air it yields α (Rose). (γ) $3MgO.2CO_2.3aq(?)$ (Fritzsche, *P.* 37, 310). Denied by Rose.

Magnesium hydrogen carbonate. $Mg.H_2(CO_3)_2$ (Soubeiran). Obtained by shaking up *magnesia alba* with CO_2Aq. The sol. has a bitter taste and alkaline reaction; becomes turbid at 75° but clears on cooling. Heated to 50°, or evaporated *in vacuo*, it yields hydrate α (*v. supra*) (Berzelius; Fritzsche).

Magnesium-ammonium carbonate. $Mg.(NH_4)_2(CO_3)_2.4H_2O$. Translucent rhombohedra, from a mixture of cold $MgCl_2Aq$, or $MgSO_4Aq$, and NH_4 sesquicarbonate solution.

Magnesium-potassium carbonates: (1) $Mg(KH).(CO_3)_2.4aq$. In large crystals from cold aqueous mixture of $MgCl_2$ or $Mg(NO_3)_2$ with excess of $KHCO_3$. The crystals at 100° become opaque, and lose water. Decomposed by water, leaving a residue $6MgCO_3.MgH_2O_2.6aq$ (Berzelius); also obtained in oblique rhombic prisms (Deville, *A. Ch.* 33, 75); (2) $MgK_2(CO_3)_2.4aq$ by digesting *magnesia alba* at 60°–70° for 12 to 15 hours with $KHCO_3Aq$ (Deville, *l.c.*).

Magnesium-sodium carbonate $MgNa_2(CO_3)_2$. Prepared in anhydrous microscopic crystals as the corresponding K salt.

On solubility of $MgCO_3$ in CO_2Aq under pressure *v.* Merkel (*J.* 1867. 136) and Wagner (*J. pr.* 102, 233). On solubility of $MgCO_3$ and $CaCO_3$ in solutions of calcium and magnesium salts, and the reactions of dolomite or gypsum and magnesite in presence of water containing CO_2 *v.* Hunt (*Am. S.* [2] 42, 49). For reactions of basic $MgCO_3$ and gypsum with CO_2Aq *v.* Gossmann (*Am. S.* [2] 42, 217, 368).

Manganese carbonate. $MnCO_3$. S. water = ·013; aqueous CO_2 = ·028 (John). Occurs native as *diallogite*, in rhombohedral crystals, isomorphous with calcite. Prepared by heating $MnCl_2Aq$ in sealed tubes to 160° with Na_2CO_3Aq, or to 140°–170° with $CaCO_3$ for 12 to 48 hours (Senarmont, *C. R.* 28, 693). $2MnCO_3.H_2O$ is obtained by drying *in vacuo* the pp. formed by alkaline carbonates with manganous salts (*Gm.* 4, 214; Prior, *Fr.* 1869. 428). Dried in air pp. contains Mn_3O_4. Equivalent quantities of Na_2CO_3 and $MnCl_2$ yield $5MnCO_3.2MnH_2O_2$ (Rose, *A.* 80, 235). $MnCO_3$ is a fine amorphous faintly rose-coloured powder. The hydrate is snow-white and tasteless. Anhydrous or hydrated the salt is permanent at ordinary temps. Heated to redness in air it yields Mn_3O_4. Strongly heated in H it yields MnO_2. In chlorine it gives $4MnCO_3 + Cl_2 = MnCl_2 + Mn_3O_4 + 4CO_2$ (Wöhler). Chlorine water, or calcium hypochlorite solution, converts it first into Mn_3O_4, and then into MnO_2. Solutions of ammoniacal salts dissolve it when freshly ppd.

Mercury carbonates. *Mercuric carbonate* unknown. Neutral or acid carbonates of K or Na yield brown red pps. $2HgO.HgCO_3$ (Setterberg, *P.* 19, 60). Mercuric chloride yields an oxychloride.

Mercurous carbonate. Hg_2CO_3. A black or yellow powder. $Hg2NO_3Aq$ is mixed with slight excess of $Na(orK)HCO_3Aq$; the mixture is set aside for a few days and frequently stirred, and the pp. then washed quickly, and dried over H_2SO_4 *in vacuo* (Setterberg, *l.c.*). Easily loses CO_2; is converted into HgO by exposure to air; blackened by alkalis with separation of Hg (*Gm.* 6, 15).

Nickel carbonate. $NiCO_3$. For preparation, *v.* COBALT CARBONATE. It is a greenish-white powder in minute rhombohedra scarcely attacked by strong acids at ordinary temperatures.

Hydrocarbonates:

(1) $NiCO_3.2NiH_2O_2.4H_2O$. Occurs native as *emerald nickel* (Silliman, *Am. S.* [2] 6, 248; Shepard, *ibid.* 250). (2) $2NiCO_3.3NiH_2O_2.4H_2O$ is the pp. obtained from cold $NiSO_4Aq$ and Na_2CO_3Aq, when dried at 100°. Boiled with water takes up water and loses CO_2. Heated above 100° in air gives off water and CO_2, and is partly converted into Ni_2O_3 (Rose, *A.* 80, 237). Not altered by digestion at 60°–70° with $NaHCO_3Aq$ (Deville). The pps. produced by alkaline carbonates in solutions of nickel salts vary with temperature, strength, and proportions, of solutions employed.

Nickel-potassium carbonates:

(1) $NiK_2(CO_3)_2.4H_2O$; shining apple-green microscopic needles. (2) $NiKH.(CO_3)_2.4H_2O$: light-green, apparently oblique rhombic prisms. Obtained similarly to corresponding cobalt salts (Deville).

Nickel-sodium carbonate,

$NiNa_2(CO_3)_2.10H_2O$ is obtained like the cobalt salt, in small prisms (Deville).

Palladium carbonate. A light yellow pp. is formed by adding solution of an alkaline carbonate to a solution of a Pd salt. No CO_2 is evolved at first, but on continuing ppn. effervescence ensues and pp. turns brown. A small quantity of CO_2 retained when dry (Berzelius).

Potassium carbonates. Two salts have been obtained.

I. *Normal carbonate*: K_2CO_3. S. 95·2 at 3°; 111 at 12°; 204 at 70°. The commercial salt is prepared by treating the ash of plants, especially of beetroot, with water, and evaporating. The residue, containing 60–80 p.c. K_2CO_3, is sold as '*crude potash*.' The impurities—KCl, K_2SO_4, and a little K silicate—are partially removed by digesting for several days with its own weight of cold water, decanting, and evaporating quickly with constant stirring. The small crystals obtained are washed with pure K_2CO_3Aq, dried, and heated to redness in metal vessels; the product is '*pearl ash*,' which usually contains from 2 to 3 p.c. impurities.

Pure K_2CO_3 is prepared (1) by heating pure K oxalate; (2) by digesting powdered cream of tartar with water containing a little HCl, washing, drying to render silica insoluble, crystallising from water to remove Na salts, heating in a closed silver dish, digesting residue with hot water, filtering, evaporating to dryness, dissolving in cold water, evaporating, and repeating treatment with cold water and evaporation two or three times (Stas, *Chem. Proport.* 340). (*v.* also Smith, *C. N.* 30, 234).

Properties and Reactions.—White solid, melting at red heat (83°) (Carnelley, *C. J.* 33, 280), volatilised without change at white heat; very deliquescent; $[K^2CO^3,Aq] = 6490$ (*Th.* 3, 198). Solution strongly alkaline; hot solution deposits rhombic octahedra $K_2CO_3.2H_2O$; conc. solution deposits monoclinic crystals $2K_2CO_3.3H_2O$, which at 100° give $K_2CO_3.H_2O$ (Städeler, *A.* 133, 371; Pohl, *W. A. B.* 41, 630). *Heated with aqueous vapour* is partly decomposed, giving KOH; *heated with charcoal* gives K and CO (*v.* POTASSIUM); *heated with sulphur* forms K sulphide and sulphate, and CO_2 (Berthelot, *Bl.* [2] 40, 362); *heated in sulphur dioxide* gives K_2SO_4 and traces of K_2S (Berthelot, *A. Ch.* [5] 30, 547). Solutions, about 1 in $10H_2O$, partly decomposed by CaO_2H_2 giving KOHAq; amount of change much increased by boiling; reverse reaction occurs with more conc. solutions.

II. *Potassium-hydrogen carbonate*: $KHCO_3$. S. 22·4 at 0°; 33·2 at 20°; 45·2 at 40°; 16·4 at 60° (Dibbits, *J. pr.* [2] 10, 417). Prepared (1) by passing CO_2 into solution of commercial normal carbonate; (2) by passing CO_2 into solution obtained by lixiviating residue from heating K-H tartrate in closed vessels, and crystallising. *Properties and Reactions.*—Large transparent monoclinic crystals, $KHCO_3.H_2O$; solution has slightly alkaline reaction, and gives off CO_2 on gently warming (*v.* Dibbits, *J. pr.* [2] 10, 417). At 200° gives K_2CO_3 and CO_2.

Rubidium carbonate Rb_2CO_3. By ppn. of Rb_2SO_4Aq with $BaOAq$, adding $(NH_4)_2CO_3$ to filtrate, evaporating to dryness, exhausting with water, and evaporating this solution, indistinct crystals of $Rb_2CO_3.H_2O$ are obtained. Soluble in alcohol, strongly alkaline. Heated, lose water and leave Rb_2CO_3, as a sandy powder, which melts at a higher temperature. In air it deliquesces, and yields $RbHCO_3$, in glassy prismatic crystals; permanent in air; having very faint alkaline reaction; easily converted by heat

into Rb_2CO_3 (Bunsen a. Kirchoff) (melting-point, 837°; Carnelley a. Williams, *C. J.* 37, 125).

Samarium carbonate $Sm_2(CO_3)_3.3H_2O$. Needles insoluble in water. The following double salts have also been prepared. *Samarium-ammonium carbonate*, $SmNH_4(CO_3)_2.2H_2O$. *Samarium-potassium carbonate*, $SmK(CO_3)_2.6H_2O$; brilliant needles. *Samarium-sodium carbonate*, $SmNa(CO_3)_2.8H_2O$; a crystalline pp. (Clève, *Bl.* [2] 43, 168).

Silver carbonate Ag_2CO_3. Prepared in crystals by adding ammonia by drops to mixed solutions of $AgNO_3$ and Na_2CO_3 of definite strength (Vögel, *J. pr.* 87, 288). As a white pp., becoming yellow on washing, by adding Na_2CO_3Aq to $AgNO_3Aq$. Blackens on exposure to light. Is readily soluble in strong NH_3Aq. Solution treated with absolute alcohol yields a pp. containing Ag_2CO_3 and ammonia (Berzelius). At 200° loses CO_2 and leaves Ag_2O. By ppg. $AgNO_3Aq$ with large excess of alkaline carbonate and boiling, a substance, possibly a mixture, is obtained which dried at 100° has formula $Ag_2CO_3.2Ag_2O$ (Rose, *A.* 81, 202). *Ammonio-silver carbonate* $Ag_2CO_3.4NH_3$. A grey pp. on adding absolute alcohol to Ag_2CO_3 dissolved in NH_3Aq (Keen, *C. N.* 31, 231).

Sodium carbonates. Three salts have been isolated, besides various hydrates, and several double salts.

I. *Normal carbonate* Na_2CO_3. Occurs in waters of several lakes and mineral waters; is a constant constituent of ash of sea-plants.

Formation.—1. From Na_2SO_4, by heating with C and $CaCO_3$, and lixiviating with H_2O (Leblanc's process).—2. From cryolite, by heating with CaO and decomposing the Na aluminate formed by CO_2.—3. By reaction between NaCl and $(NH_4)_2CO_3$ in solution.

Preparation.—1. Soda crystals are repeatedly washed with cold water until all sulphates, chlorides, &c. are removed; the last traces of SiO_2 are removed by dissolving the washed salt in water, evaporating nearly to dryness, adding a little $(NH_4)_2CO_3$, heating till quite dry, dissolving in water, filtering, evaporating, and heating (Wurtz, *J.* 1852. 357).—2. Soda crystals are repeatedly recrystallised, the crystals being obtained as small as possible (Gay-Lussac, *A.* 12, 15); most of the chlorides and sulphates and iron salts are thus removed. The washed salt is dried, heated in a silver dish, and the residue is repeatedly washed with small quantities of cold water; the salt is now free from iron, but may contain traces of silica (*v. supra*) (Stas).

Properties and Reactions. — White solid; melts at c. 818° (Carnelley, *C. J.* 33, 280), giving off a little CO_2 (Jacquelain, *A. Ch.* [3] 32, 205; Mallard, *A. Ch.* [4] 28, 86; Scheerer, *A.* 116, 134). Heated in steam gives NaOH. Decomposed at high temperature by *carbon*, to Na and CO; by *phosphorus*, to C, CO, and Na orthophosphate (Dragendorff, *C. C.* 1861. 865); by *silicon* to C, CO, and Na silicate; by *sulphur*, at 275°, to Na_2S and $Na_2S_2O_3$, at melting-point, to Na_2S_x and Na_2SO_4; by *ferric oxide*, or *ferrous oxide*, with evolution of CO_2 (Stromeyer, *A.* 107, 366); by *ferrous sulphide* to Na and Na-Fe sulphide (E. Kopp, *Bl.* [2] 5, 207). *Solubility* in water increases from 0° to 34°; from 34° to 79° S. is constant: S. = 46·2 at 34° (Löwel, *A. Ch.* [3] 33, 353; Poggiale, *A. Ch.* [3] 8, 468; Tomlinson, *C. N.* 18, 2; Gerlach, *Fr.* 8, 279). Solution is accompanied with production of heat; $[Na^2CO^3, Aq] = 5,640$ (*Th.* 3, 198).

Hydrates of Na_2CO_3.—(1) $Na_2CO_3.10H_2O$; separates from moderately conc. solutions at ordinary temperatures, in clear, monoclinic crystals; these melt at c. 34°, leaving $Na_2CO_3.H_2O$ (Schindler, *Mag. Pharm.* 33, 14); according to Thomsen (*B.* 11, 2012) the residue is $Na_2CO_3.2H_2O$ but this gives up another H_2O in the air. Crystals of $Na_2CO_3.10H_2O$ effloresce in air; at 12·5° they give the hydrate with $5H_2O$; and at 38° *in vacuo*, or over $CaCl_2$, the hydrate $Na_2CO_3.H_2O$ (Watson, *P. M.* 12, 130). Dissolve in water with disappearance of heat $[Na^2CO^3.10H^2O, Aq] = -16,160$ (*Th.* 3, 198).

(2) $Na_2CO_3.15H_2O$ (Jacquelain, *A. Ch.* [3] 32, 205). Crystallises from conc. solutions of Na_2CO_3 at −20°.

(3) $Na_2CO_3.7H_2O$ (Löwel, *A. Ch.* [3] 33, 353; Rammelsberg; Marignac, *Ann. M.* [5] 12, 55). Crystallises from hot saturated solutions by cooling in closed vessels; if air has entrance the $10H_2O$ hydrate forms. Said to crystallise in two modifications, rhombohedra and rhombic tables, with different solubilities.

(4) $Na_2CO_3.6H_2O$; crystallises from Na_2SAq standing in air, also from NaClAq mixed with K_2CO_3Aq (Mitscherlich, *P.* 8, 441).

(5) $Na_2CO_3.5H_2O$; crystallises at temperatures over 33° from molten $Na_2CO_3.10H_2O$ (Berzelius, *P.* 32, 303); also by the efflorescence of $Na_2CO_3.10H_2O$ at 12·5°.

(6) $Na_2CO_3.2H_2O$; melting $Na_2CO_3.10H_2O$ at 34° (Thomsen); $[Na^2CO^3.2H^2O, Aq] = 20$.

(7) $Na_2CO_3.H_2O$; from hot saturated solutions of Na_2CO_3, or from hot solutions of $Na_2CO_3.10H_2O$; separates from boiling solutions; also produced by efflorescence of some of the hydrates with more H_2O (Marignac, *Ann. M.* [5] 12, 55; Haidinger, *P.* 5, 369). $[Na^2CO^3.H^2O, Aq] = 2,250$ (*Th.*).

II. *Sodium-hydrogen carbonate*; $NaHCO_3$ (*Bicarbonate of soda*). *Formation.*—1. By passing NH_3 into NaClAq, and then decomposing by CO_2 under pressure;

$$NH_3 + NaClAq + CO_2 + H_2O =$$
$$NaHCO_3 + NH_4ClAq$$ (Ammonia soda process).—2. By reaction between soda crystals in solution and commercial NH_3 carbonate.—3. By reaction between CO_2 and effloresced soda crystals, or a mixture of 1 part crystallised and 3 parts dry Na_2CO_3.—4. By passing CO_2 into Na_2CO_3Aq as long as it is absorbed (1 part Na_2CO_3 in 2 parts H_2O) (L. Meyer, *A. Suppl.bd.* 2, 170; Berzelius, *P.* 16, 434; Mohr, *A.* 19, 15; 29, 268). *Properties and Reactions.*—White monoclinic tables; alkaline taste; changes moist red litmus to blue, but has no action on colour of turmeric paper. In moist air readily goes to $Na_2CO_3.xaq$. When heated gives off CO_2 and H_2O; solution decomposed on boiling (Rose, *P.* 34, 158). S. 8·8 at 10°; 14·64 at 70° (Poggiale, *A. Ch.* [3] 8, 468; also Dibbits, *J. pr.* [2] 10, 417).

III. *Sesquicarbonate.* $Na_4H_2(CO_3)_3.3H_2O$ ($= Na_2CO_3.2NaHCO_3.3H_2O$). Occurs native; S.G. 2·112. Prepared (1) by heating $NaHCO_3$ to 200° (Hermann, *J. pr.* 26, 312); (2) by evapo-

rating solutions of $NaHCO_3$ *in vacuo* over H_2SO_4; (3) by melting together the two carbonates, in the ratio $Na_2CO_3.10H_2O:2NaHCO_3$, and standing in air till mass becomes crystalline, when it contains crystals of the sesquicarbonate; (4) by pouring alcohol on to a mixture of Na_2CO_3Aq and $NaHCO_3$, the salt separates in fine needles (Winkler, *R. P.* 48, 215). Monoclinic crystals; non-efflorescent in air, goes to Na_2CO_3 at red heat; aqueous solution *in vacuo* over H_2SO_4 gives Na_2CO_3 and $NaHCO_3$ (Rose, *P.* 34, 160). S. 12·63 at 0°; 41·59 at 100° (Poggiale).

IV. *Double Salts.* Sodium-potassium carbonates.

(1) $NaKCO_3.6H_2O$; monoclinic crystals, unchanged in dry air, effloresces in moist air; by evaporating solution of equal equivalents of the constituent salts, and crystallising from K_2CO_3Aq. At 100° loses $6H_2O$. S. 185 at 15° (Marignac, *C. R.* 45, 650; Marguerite, *A.* 56, 220; Stolba, *Bl.* [2] 4, 192, 7, 241).

(2) $2Na_2CO_3.K_2CO_3.18H_2O$; from mother-liquor from which $K_4Fe(CN)_6$ has crystallised out. May be crystallised from K_2CO_3Aq (Marguerite).

Sodium-calcium carbonate: $Na_2CO_3.CaCO_3.5H_2O$; occurs native as *Gay-Lussite*; obtained, in microscopic monoclinic crystals, by reaction between freshly ppd. $CaCO_3$ and conc. Na_2CO_3Aq at ordinary temperature. When dry this compound is decomposed by water (Fritzsche, *J. pr.* 93, 339; Boussingault, *P.* 7, 97; H. Rose, *P.* 93, 606).

Strontium carbonate. $SrCO_3$. S.G. (pp.) = 3·62. S. (cold or hot) = ·0003 (Bineau, *C. R.* 41, 509). S. (cold) = ·005 (Fresenius) solubility diminished by NH_3Aq or $(NH_4)_2CO_3Aq$. S. (10° in satd. CO_2Aq) = ·12 (Lassaigne). Occurs native as *strontianite*. Crystals of trimetric system, isomorphous with arragonite and witherite. Prepared by ppn. with an alkaline carbonate as a smooth white substance; in form of strontianite, by crystallising amorphous carbonate from fused KCl and NaCl (Bourgeois, *Bl.* [2] 37, 447). Heated in closed vessel CO_2 given off only at about white heat, but in aqueous vapour SrH_2O_2 is formed at a much lower temp. Alkaline sulphates in solution do not decompose it at any temperature (Rose, *P.* 95, 284). Ammonium chloride solution boiled with it converts it into $SrCl_2$.

Thallium carbonate Tl_2CO_3. S.G. (fused) 7·06 (Lamy). S. (15·5°) = 4·02; (60°) = 11·7; (100°) = 27·21. M.P. c. 272° (Carnelley, *C. J.* 33, 275). Formed by exposure of Tl in a saturated solution of Tl_2O to air. Prepared by allowing granulated metal to oxidise in warm air, boiling with water containing excess $(NH_4)_2CO_3$ and filtering. Tl_2CO_3 is deposited in groups of prisms (Miller, *Pr.* 14, 555), which are brilliant, highly refractive, very heavy, anhydrous, colourless; melting, undecomposed, much below redness to clear liquid which solidifies to dark-grey mass, and at red heat decomposes evolving CO_2. Taste mildly caustic and metallic. Solution has alkaline reaction not completely removed by supersaturation with CO_2 (Crookes; Werther, *J.* 1864. 249).

Thorium carbonate. $Th(CO_3)_2.3ThH_4O_4.2H_2O$. Alkaline carbonates throw down a basic salt with evolution of CO_2. Moist ThH_4O_4 absorbs CO_2 from air. ThO_2 is not sol. in water containing CO_2 (Berzelius). Salt of above formula obtained as an amorphous pp. by treating hydrate suspended in water with CO_2, or by ppg. solution of $ThCl_4$ with an alkaline carbonate.

Tin carbonates. $SnCO_3.SnO$; by adding solid $SnCl_2$ to conc. Na_2CO_3Aq in absence of air: very unstable. If $(NH_4)_2CO_3Aq$ is used, hexagonal prisms of $(NH_4)_2O.2SnO.3CO_2.3H_2O$ are said to be formed (Deville, *A. Ch.* [3] 35, 448).

Uranium carbonates have not been isolated. Alkaline carbonates ppt. uranous hydrate from UCl_4, a basic sulphate from $U(SO_4)_2$, and double carbonates from uranic salts.

Uranyl-ammonium carbonate. $(UO_2)CO_3.2(NH_4)_2CO_3$. S. = 5 at 15°; increased by $(NH_4)_2CO_3$. Prepared, in small yellow transparent crystals, by digesting in $(NH_4)_2CO_3Aq$ at 60°–80° the pp. produced by NH_3Aq or $(NH_4)_2CO_3Aq$ from uranic salts, filtering, and allowing to cool. Decomposed slowly at ordinary, more quickly at higher, temps. leaving UO_3; solution boiled evolves NH_3 and CO_2, and deposits yellow pp., containing uranium, of doubtful composition (Arfredson, Péligot; Ebelmen, *A. Ch.* [3] 5, 189; Delffs, *P.* 55, 229).

Uranyl-potassium carbonate. $(UO_2)CO_3.2K_2CO_3$. S. = 7·4 at 15°; insol. in alcohol. Prepared, as a bright yellow crystalline crust, by dissolving in $KHCO_3Aq$ the pp. formed from uranic salts by K_2CO_3Aq, and evaporating. At 300° evolves CO_2; at red heat leaves mixture of K uranate and carbonate. KOHAq pps. all the U as K uranate, even in presence of excess of K_2CO_3.

Uranyl-sodium carbonate. $(UO_2)CO_3.2Na_2CO_3$. Preparation and properties similar to K salt. Two Ca salts,

(1) $(UO_2)CO_3.CaCO_3.10H_2O$;
(2) $(UO_2)CO_3.CaCO_3.5H_2O$;

occur native (Smith, *A.* 66, 253).

Yttrium carbonate. $Y_2(CO_3)_3$. Na_2CO_3Aq pps. it from yttrium salts with $12H_2O$ in the cold, and $3H_2O$ at 100°. Not easily decomposed by heat; sparingly soluble in water containing CO_2. Solution in $(NH_4)_2CO_3Aq$, if concentrated, deposits a white crystalline double salt which does not redissolve in $(NH_4)_2CO_3Aq$; also soluble in K_2CO_3 and Na_2CO_3Aq (Berzelius).

Zinc carbonate. $ZnCO_3$. Occurs as *calamine*. Not obtained by precipitation. Pp. formed by $KHCO_3Aq$ in $ZnSO_4Aq$ is $2ZnCO_3.3ZnO_2H_2$ (Berzelius). $ZnCO_3$ unaltered at 200°; slowly evolves CO_2 at 300° (Rose).

Hydrocarbonates. Native hydrocarbonates are (1) *zinc bloom* $ZnO.ZnCO_3.3ZnH_2O_2$ (Berzelius), or $ZnCO_3.2ZnH_2O_2$4aq (Smithson a. Borndorff, *Gm.* 6, 15). (2) *Auricalcite* or *green calamine* $2ZnCO_3.3ZnH_2O_2$, in which Zn is partly replaced by Cu. (3) *Buratite*, a hydrocarbonate containing Cu and Ca.

The pps. formed by alkaline carbonates in solutions of zinc salts all appear to contain water, and to vary in composition with strength, temperature, and proportions, of solutions. For results obtained under varying conditions, *v.* Rose (*P.* 85, 107), Schindler a. Boussingault (*Gm.* 1, 15). They all evolve CO_2 and H_2O at 200°, yielding ZnO (Rose).

Ammonio-carbonate of zinc $(NH_3Zn)CO_3$. Deposited in crystals from a solution of ppd. zinc carbonate in conc. $(NH_4)_2CO_3Aq$ (Favre, *Traité de Chimie*, Pelouze et Frémy, 2nd ed. 8, 47).

Zinc-potassium carbonate
$8ZnCO_3.3K_2CO_3.7H_2O$ (?). Crystallises from a solution of $ZnCl_2$ mixed with K sesquicarbonate (Deville, *A. Ch.* [3] 32, 75).

Zinc and sodium carbonate
$8ZnCO_3.3Na_2CO_3$ (?). Small crystals, obtained as potassium salt (Deville).

Zirconium carbonate. Excess of alkaline carbonate solution produces a pp. in solutions of Zr salts, soluble in Na_2(orK_2)CO_3Aq. Composition seems to be variable (Hermann, Klaproth, Vauquelin).

THIO-CARBONIC ACID. H_2CS_3. Mol. w. unknown. A dark yellow very strongly smelling oil; obtained by adding cold dilute HClAq to K_2CS_3 or Na_2CS_3; very easily decomposed, by heating, to CS_2 and H_2S (Zeise, *S.* 41, 105; Berzelius, *P.* 6, 450).

THIO-CARBONATES. These salts have the composition M_2CS_3, or MCS_3, when $M_2 = Na_2$ &c., and M = Ca &c. A few *basic* salts are also known. The composition of the salts of the alkali and alkaline earth metals has been determined; several other thio-carbonates seem to be produced in the reactions between solutions of metallic salts and K_2CS_3Aq or Na_2CS_3Aq, but the composition of very few of these thio-carbonates of the heavy metals has been determined. Thio-carbonates are formed by reactions between CS_2 and aqueous solutions of the monosulphides of the alkali and alkaline earth metals, M_2S and MS. By using MOHAq and CS_2, thio-carbonates and carbonates are formed simultaneously; with MO_2H_2Aq and CS_2 (M = Ca,Ba,Sr) *basic* thio-carbonates are formed, *e.g.* $CaCS_3.2CaO_2H_2.6H_2O$. NH_4Aq reacts with CS_2 to form $(NH_4)_2CS_3$ and $(NH_4)CNS$ (Gélis, *J.* 1861. 340). The thio-carbonates are yellow, red-yellow, brown, or black, solids; the hydrated salts are yellow. The salts of the alkali and alkaline earth metals are soluble in water; those of the heavy metals are more or less soluble in excess of M_2CS_3Aq (M = Na &c.). The thio-carbonates are not very stable; those of the heavy metals easily decompose to metallic sulphide and CS_2; conc. solutions of the alkali salts change to H_2S and alkali carbonates when boiled, dilute solutions decompose by standing in air to carbonates and S. Heated alone, most of them give metallic sulphide and CS_2; K_2CS_3 gives K_2S_3 and C. The thio-carbonates have been chiefly investigated by Zeise (*S.* 41,105); Berzelius (*P.* 6, 450); Walker (*C. N.* 30, 28); Sestini (*G.* 1871. 473; *B.* 5, 327); Gélis (*J. Ph.* [3] 39, 95; *C. R.* 81, 282); P. Thénard (*C. R.* 79, 673); Husemann (*A.* 123, 67); Mermet (*C. R.* 81, 344).

Ammonium thiocarbonate $(NH_4)_2CS_3$. Prepared by mixing a saturated alcoholic solution of NH_3 with $\frac{1}{10}$ its vol. CS_2, cooling after the liquid has become brown, pouring off liquid, and washing the crystals several times with alcohol, then with ether, and pressing between paper (Zeise). Yellow crystals, v. sol. in water, insol. in alcohol or ether; may be sublimed in dry air by gentle warming; very hygroscopic. Aqueous solution heated to 90°-100° evolves H_2S, and NH_4CNSAq remains (Gélis).

Barium thiocarbonate $BaCS_3$. By shaking BaSAq with CS_2, washing with alcohol, and drying *in vacuo*.

Calcium thiocarbonate. $CaCS_3$. By digesting CaS with excess of CS_2, and evaporating *in vacuo*. Citron-yellow; sol. in alcohol or water; milk of lime shaken with CS_2 gives an orange-red pp. of $CaCS_3.2CaO_2H_2.6H_2O$, and this at 30° gives red liquid from which red crystals of $CaCS_3.3CaO_2H_2.7H_2O$ separate (Walker; Sestini).

Potassium thiocarbonate. K_2CS_3. When K_2SAq is digested with CS_2 at 30° in a closed vessel, or CS_2 is dissolved in a conc. alcoholic solution of K_2S, yellow deliquescent crystals separate; dried at 60°-80° these give K_2CS_3, a red-brown solid; v. sol. in water, sl. sol. in alcohol.

The other thiocarbonates which have been fairly well examined and analysed are those of **Lithium, Magnesium, Sodium,** and **Strontium.** Thiocarbonates of Bi, Cd, Cr, Co, Au, Fe, Pb, Mn, Hg, Ni, Pt, Ag, Sn, Zn, seem also to be formed by adding the solution of an alkali thiocarbonate to a solution of a salt of each of these metals. M. M. P. M.

CARBONIC ANHYDRIDE CO_2 *v.* CARBON, OXIDES OF.

CARBON TETRA-CHLORIDE *v. supra* and TETRA-CHLORO-METHANE.

CARBONIC ETHERS. There are three classes of carbonic ethers: viz. acid ethers CO(OR)(OH), normal ethers $CO(OR)_2$, and ethers of ortho-carbonic acid $C(OR)_4$. In these formulæ R may be any alkyl. They are described as salts of the alkyl: *e.g.* ETHYL CARBONATE, METHYL CARBONATE, PHENYL CARBONATE, &c.

Orthocarbonic ethers are formed by the action of sodium alcoholates on chloropicrin (Williamson a. Basset, *A.* 132, 54). They are converted by ammonia into guanidine.

Normal carbonic ethers.

Formation. — 1. From alkyl iodides and silver carbonate (de Clermont, *A.* 91, 375).— 2. By the action of Na, K, solid NaOEt (½ mol.) or KOEt (½ mol.), upon alkyl oxalates (1 mol.) (Ettling, *A.* 19, 17; Löwig a. Weidmann, *A.* 36, 301; Geuther, *Z.* 1868, 656; Cranston a. Dittmar, *Z.* 1870, 4).—3. By the action of alkyl chloroformates upon sodium alcoholates, *e.g.*:
Cl.CO.OEt + NaOMe = NaCl + MeO.CO.OEt
(Roese, *A.* 205, 240). The mixed ether prepared from ethyl chloroformate and sodium methylate is identical with that from methyl chloroformate and sodium ethylate.—4. From $COCl_2$ and sodium alcoholates.

Properties.—The boiling-points and specific gravities of the fatty carbonic ethers are as follows (Roese, *A.* 205, 244):—

Ether	Boiling-point	S.G.
Me_2CO_3	90·6°	1·065 at 17°
$MeEtCO_3$	109·2°	1·00 at 27°
Et_2CO_3	125°	·97
$MePrCO_3$	130·8°	·98 at 27°
Pr_2CO_3	168·2°	·95 at 17°
$Me(PrCH_2)CO_3$	143·6°	·95 at 27°
$Et(PrCH_2)CO_3$	160·1°	·93 at 27°
$(PrCH_2)_2CO_3$	190·3°	·92 at 15°
$Et(C_5H_{11})CO_3$	182·3°	·92 at 27°
$(C_5H_{11})_2CO_3$	228·7°	·91 at 15°

Reactions.—1. *Ammonia* converts the ethers R_2CO_3 into carbamic ethers, and finally into urea.—2. PCl_5 forms chloroformic ethers. In mixed ethers $RR'CO_3$ the alkyl which is converted into chloride is the smaller of the two: $Et(C_5H_{11})CO_3 + PCl_5 = EtCl + ClCO_2C_5H_{11} + POCl_3$ The amides of the chloroformates, which may be regarded as half chloride half amide of carbonic acid (carbamic chlorides), are obtained by the action of $COCl_2$ upon the hydrochlorides of amines, *e.g.* $COCl_2 + NEtH_2 = COCl(NEtH) + HCl$ (Gattermann a. Schmidt, *B.* 20, 118) *cf.* CHLOROFORMIC ACID.—3. When an alkyl carbonate is heated with an alcohol containing a heavier alkyl, the heavy alkyl displaces the light one (R.).

Chloro-imido-carbonic ethers $ClN:C(OR)_2$. These are formed by leading chlorine into a cooled solution of NaOH and KCN in an alcohol (Sandmeyer, *B.* 19, 862). They are crystalline, and converted by dilute acids or by aqueous H_2S into the corresponding carbonic ethers. Aqueous potassium arsenite reduces them to imido-carbonic ethers (*cf.* CHLORO-IMIDO-CARBONIC ETHERS).

Imido-carbonic ethers $HN:C(OR)_2$. Prepared as above, are alkaline liquids, readily decomposed by aqueous acids into NH_3 and carbonic ethers (*cf.* IMIDO-CARBONIC ETHERS).

CARBO-DI-NICOTINIC ACID *v.* PYRIDINE TRI-CARBOXYLIC ACID.

CARBONIC OXIDE. Name usually given to CO, *v.* CARBON, OXIDES OF.

CARBONIC - OXIDE - POTASSIUM *v.* potassium salt of HEXA-OXY-BENZENE.

CARBONOUS OXIDE CO, *v.* CARBON, OXIDES OF.

CARBON TETRA-IODIDE *v.* TETRA-IODO-METHANE.

CARBONPIMELIC ACID *v.* *iso*-PENTANE TRI-CARBOXYLIC ACID.

CARBONYL. The divalent radicle C:O. When attached to two carbon atoms the product is a ketone, when attached to one carbon atom and to hydroxyl the compound is a carboxylic acid; when attached to one carbon atom and to one hydrogen atom the product is an aldehyde. Two or three carbonyls attached to CH render the hydrogen displaceable by metals. Many carbonyl derivatives of amido- compounds are described under the amido- compounds from which they are formed by the action of $COCl_2$.

CARBONYL - DI - *m* - AMIDO - DI - BENZOIC ACID *v.* DI-PHENYL-UREA-DI-*m*-CARBOXYLIC ACID.

CARBONYL - AMIDO - PHENOL *v.* *Anhydride of* OXY-PHENYL-CARBAMIC ACID.

CARBONYL BROMIDE *v.* CARBON, OXY-BROMIDE OF.

CARBONYL DI-BIURET *v.* BIURET.

CARBONYL-CARBAMIC ETHER $C_4H_5NO_3$ *i.e.* CO:N.CO.OEt or $(C_4H_5NO_3)_3$. *Carboxethyl cyanate* or *cyanurate.* [119°]. Formed by the action of chloroformic ether on potassium cyanate. If dry ether be present a second compound $C_{10}H_{15}N_3O_5$ [107°] is also formed. Rhombic plates, sl. sol. cold alcohol, v. sol. $CHCl_3$. When heated with water to 100° it loses CO_2 forming cyanuric ether. Its formula should therefore possibly be trebled. The compound $C_{11}H_{15}N_3O_7$ when distilled with water behaves similarly (Wurtz a. Henniger, *C. R.* 100, 1419; *A. Ch.* [6] 7, 132).

Compounds with cyanic ether

(*a*) $C_{10}H_{15}N_3O_5$ or $(CO:NCO_2Et)(CO.NEt)_2$ [107°]. Formed as above, or together with carboxy-carbamic (imido-diformic) ether [50°], (226°) when the ether is wet. Needles, which lose CO_2 on heating, yielding cyanuric ether (W. a. H.).

(*b*) $C_{11}H_{15}N_3O_7$ *i.e.* $(CO.N.CO_2Et)_2(CONEt)$. [123°]. Formed together with imido-diformic ether when KCNO acts on an aqueous ethereal solution of chloroformic ether for a long time. On distilling it forms cyanuric ether (W. a. H.).

CARBONYL CHLORIDE *v.* CARBON, OXYCHLORIDE OF.

CARBONYL-GUANIDINE *v.* AMIDO-DICYANIC ACID.

CARBONYL DI-PHENYLENE *v.* DIPHENYLENE KETONE.

CARBONYL-DI-PHENYL OXIDE *v.* DIPHENYLENE KETONE OXIDE.

CARBONYL-PYRROLE $C_9H_8N_2O$ *i.e.* $OC\langle\begin{smallmatrix}NC_4H_4\\NC_4H_4\end{smallmatrix}$. *Di-tetrol-urea.* [63°]. (c. 238°). Formed, together with di-pyrryl-ketone, by the action of carbonyl chloride upon pyrrol-potassium (Ciamician a. Magnaghi, *B.* 18, 414; 1829). Large monoclinic crystals, *a*:*b*:*c* = 1·1688:1:·7189. V. sol. alcohol and ether, insol. water. By heating to 250° it is transformed into a mixture of pyrroyl-pyrrol $C_4H_4N.CO.C_4H_3NH$ and di-pyrryl-ketone $CO(C_4H_3NH)_2$.

CARBONYL SULPHIDE *v.* CARBON, OXYSULPHIDE OF.

CARBONYL-UREA *v.* UREA.

CARBOPETROCENE *v.* PETROCENE.

CARBO - DIPHENYLENE *v.* DIPHENYLENE KETONE.

CARBO-DIPHENYLIMIDE *v.* DI-PHENYL-CYANAMIDE.

CARBO-TRI-PHENYL-TRIAMINE *v.* DI-PHENYL-AMIDO-BENZAMIDINE.

CARBO-PHENYL-TOLYL-IMIDE *v.* PHENYL TOLYL CYANAMIDE.

CARBO-DI-PROPYL-DI-PHENYL-IMIDE *v.* DI-PROPYL-DI-PHENYL-CYANAMIDE.

CARBO - PYRIDENIC ACIDS *v.* PYRIDINE CARBOXYLIC ACIDS.

CARBO-PYROTRITARIC ACID *v.* DI-METHYL-FURFURANE CARBOXYLIC ACID.

CARBO-PYRROLIC ACID *v.* PYRROL-CARBOXYLIC ACID.

CARBO-PYRROLYL-FORMIC ACID *v.* PYRRYL-GLYOXYLIC ACID.

CARBOSTYRIL C_9H_7NO *i.e.* $C_6H_4\langle\begin{smallmatrix}CH:CH\\|\\NH.CO\end{smallmatrix}$ or $C_6H_4\langle\begin{smallmatrix}CH:CH\\|\\N = C(OH)\end{smallmatrix}$. *Lactam or lactim of o-amido-cinnamic acid.* (*Py*-3)-*Oxy-quinoline.* [199°].

Formation.—1. By boiling *o*-amido-cinnamic acid with HClAq (Chiozza, *C. R.* 34, 598; *A.* 83, 117; Tiemann a. Oppermann, *B.* 13, 2070).—2. Obtained by reducing tri-chloro-oxy-quinoline with HI (Rotheit, *J. pr.* [2] 29, 300).

Preparation. — *o*-Nitro-cinnamic ether is heated with alcoholic $(NH_4)_2S$ to 100° under pressure, the solution is evaporated to dryness, taken up with NaOH and the carbostyril pp.

by CO_2 (Friedländer a. Ostermeyer, *B.* 14, 1916).

Properties.—Prisms (from alcohol); or long thin threads (containing aq) from dilute aqueous solution. May be sublimed. V. sl. sol. cold, v. sol. hot, water. Sol. alcohol and ether. Alkaline $KMnO_4$ oxidises it to isatin and oxal-oxyl-amido-benzoic acid (carbostyrilic acid). $CO_2H.C_6H_4.NH.C(OH)_2.CO_2H$ [200°].

Salts.—The K and Na salts form easily soluble plates. The barium salt A'_2Ba: sparingly soluble plates.

Methyl ether: (247° uncor.). Colourless liquid. Smells of oranges.

Ethyl ether: [below 0°]. (256°). Prepared by the action of ethyl iodide on sodium-carbostyril, or of alcoholic KOH on chloro-quinoline. Volatile with steam. Colourless liquid. Sweet smell.—B'HCl: hygroscopic crystals.

Phenyl ether: [69°]. Sublimable. Glistening plates. Sol. ordinary solvents (Friedländer a. Ostermayer, *B.* 15, 335).

Reference.—AMIDO-CARBOSTYRIL, BROMO-CARBOSTYRIL, &c. Hydrocarbostyril is described under AMIDO-PHENYL-PROPIONIC ACID. Ethyl-pseudo-carbostyril is described as (*Py.* 3, 4)-OXY-ETHYL-QUINOLINE.

CARBOSTYRIL-CARBOXYLIC ACID *v.* OXY-QUINOLINE-CARBOXYLIC ACID.

CARBOTHIALDINE $C_5H_{10}N_2S_2$. Crystals which separate on adding CS_2 to an alcoholic solution of aldehyde-ammonia (Redtenbacher a. Liebig, *A.* 65, 43). Also from aldehyde and ammonic thio-carbamate (Mulder, *A.* 168, 235). Insol. water. Sol. acids.

Reactions.—1. HCl splits it up into aldehyde, NH_3 and CS_2.—2. $KMnO_4$ forms H_2SO_4, CO_2, KCy, and acetic acid.—3. HCl and Fe_2Cl_6 forms NH_4Cl, aldehyde, and $NH_2.CS.S_2.CS.NH_2$ (Guareschi, *G.* 8, 246; *B.* 11, 1383).

CARBO-TRI-THIO-HEXABROMIDE *v.* HEXA-BROMO-DI-METHYL TRI-SULPHIDE.

CARBO-TOLYLENE-DI-PHENYL-TETRA-MINE *v.* DI-PHENYL-TOLYLENE-TETRA-AMIDO-METHANE.

CARBO-DI-TOLYL-IMIDE *v.* DI-TOLYL-CYAN-AMIDE.

DICARBOTHIONIC ETHER $S(CO_2Et)_2$. (180°). From $ClCO_2Et$ and alcoholic Na_2S. Oil; decomposed by baryta-water or alcoholic KOH into Et_2S and CO_2 (V. Meyer, *B.* 2, 298).

CARBO-VALERTHIALDINE $C_{11}H_{22}N_2S_2$. [109°]. (G.); [117°] (S.). V.D. 60. From iso-valeric aldehyde (5g.), CS_2 (3g.) and aqueous NH_3 (Schröder, *B.* 4, 469). From isovaleric aldehyde and ammonium thio-carbamate (Mulder, *A.* 168, 237). Colourless needles (from alcohol). Fe_2Cl_6 on warming gives the sulphocyanide reaction. $KMnO_4$ forms HCN, H_2SO_4 and valeric acid. Fe_2Cl_6 and HCl form in the cold a yellow powder $(S.CSNH_2)_2$. Carbovaleraldine may therefore be dithiocarbamate of di-valerylidene ammonium $H_2N.CS.SN(CH.CH_2.CHMe_2)_2$ (Guareschi, *A.* 222, 310; *G.* 13, 500).

CARBOVINIC ACID is *Hydrogen* ETHYL CARBONATE (*q.v.*).

CARBOXAMIDO-BENZOIC ACID *v.* DI-PHENYL-UREA DI-CARBOXYLIC ACID.

CARBOXAMIDO-CARBIMIDAMIDO-BENZOIC ACID *v.* p. 157.

CARBOXAMIDO-CYANAMIDO-BENZOYL *v.* p. 155.

CARBOXAMIDO-HIPPURIC ACID *v.* p. 164.

CARBOXAMIDO-o-OXY-BENZOIC ACID $C_{15}H_{12}N_2O_7$. A product of the action of urea on amido-salicylic acid at 200° (Griess, *J. pr.* [2] 1, 235). Minute needles, v. sl. sol. most solvents.

CARBOXETHYL CYANATE or CYANURATE *v.* CARBONYL-CARBAMIC ETHER.

CARBOXY-ACETO-GLUTARIC ACID *v.* METHYL PROPYL KETONE TRI-CARBOXYLIC ACID.

ν-CARBOXY-o-AMIDO-BENZOIC ACID *v.* ISATOIC ACID.

ν-Carboxy-*m*-amido-benzoic ether *v.* p. 157.

CARBOXY-BENZENE PHOSPHONIC ACID $CO_2H.C_6H_4.PO(OH)_2$. [above 300°]. Prepared by the oxidation of *p*-toluene phosphonic acid $C_6H_4(CH_3).PO(OH)_2$ with $KMnO_4$. Needles or tables. V. sol. water, m. sol. aqueous HCl or alcohol. On heating to 300° it decomposes, giving metaphosphoric and benzoic acids.

Salts.—$A'''Ag_3$: slightly soluble pp.—$A'''H_2K$aq: fine needles sol. water, sl. sol. alcohol.—A'''_2H_3K: long prisms sl. sol. water.

Chloride $C_6H_4(COCl)(POCl_2)$. [83°]. (315°). Colourless crystals. Heated with PCl_5 it gives *p*-chlorobenzoyl chloride PCl_3 and $POCl_3$.

Trimethyl ether $A'''Me_3$: thick liquid (Michaelis a. Panek, *B.* 14, 405).

CARBOXY-BENZOYL-ACETIC ACID *v.* ACETOPHENONE DI-CARBOXYLIC ACID, p. 37.

CARBOXY-BENZOYL-AMIDO-BENZOIC ACID *v.* PHTHALOXYL-AMIDO-BENZOIC ACID.

CARBOXY-BENZOYL-ETHENYL TRI-CARBOXYLIC ACID *v.* PHENYL-ETHYL-KETONE TETRA-CARBOXYLIC ACID.

CARBOXY-BENZOYL-PROPIONIC ACID $C_{11}H_{10}O_5$ *i.e.* $CO_2H.C_6H_4.CO.C_2H_4.CO_2H$. The free acid is unstable, but its Na salt is formed by dissolving phthalyl-propionic acid in NaOHAq (Gabriel a. Michael, *B.* 11, 1680).

o-CARBOXY-BENZYL-ACETO-ACETIC ETHER $C_{14}H_{16}O_5$ *i.e.* $CO_2H.C_6H_4.CH_2.CHAc.CO_2Et$. [92°]. Formed by reducing phthalyl-aceto-acetic ether with zinc-dust in glacial acetic acid (Bülow, *A.* 236, 190). Needles; v. sol. hot water, alcohol, ether, and HOAc. The ammonium salt melts at [121°]. Boiling baryta-water converts it into benzyl-acetone *o*-carboxylic acid.

Phenyl hydrazide $C_{20}H_{22}N_2O_4$. [235°]. Decomposes slowly forming alcohol and $C_{18}H_{16}N_2O_3$ [239°].

o-CARBOXY-BENZYL-MALONIC ACID $HO_2C.C_6H_4CH_2.CH(CO_2H)_2$. Formed by saponifying *o*-carboxy-benzyl-malonic ether (Wislicenus, *A.* 242, 37). Prisms. V. sol. hot, sl. sol. cold, water. Heated to 190° gives off CO_2 and forms *o*-carboxy-phenyl-propionic acid [166°].

Salt.—$A'''Ag_3$. V. sl. sol. hot water.

Di-ethyl ether $CO_2H.C_6H_4.CH_2.CH(CO_2Et)_2$. [86°]. S. ·045 at 17°. Formed by reducing phthalyl malonic ether with acetic acid and zinc (Wislicenus, *A.* 242, 32). Fine needles. V. e. sol. ether and hot alcohol, sl. sol. hot water.

Salts.—A'Ag: white needles.—A'Na: deliquescent needles. V. sol. alcohol, insol. ether.

Tri-ethyl-ether $A'''Et_3$. (250°) at 45 mm.

CARBOXY-CARBAMIC ETHER $C_6H_{11}NO_4$ *i.e.* $NH(CO_2Et)_2$. [50°]. (226°).

Formation.—1. By the action of chloroformic ether on potassium cyanate in the presence of wet ether. A second compound $C_{10}H_{15}N_3O_7$ [107°], insoluble in water, is also formed, while a small quantity of yellow oil [170°] is found in the aqueous extract. If absolute alcohol be used instead of ether, the second compound is not formed.—2. Chloroformic ether (34 gr.) and carbamic ether (24 gr.) are heated together at 120°.

Properties.—Long prisms. It forms biuret and alcohol when made with aqueous NH_3. The salt $C_6H_{10}NO_4Ag$ crystallises in cubes (Wurtz a. Henniger, *A. Ch.* [5] 7, 135).

CARBOXY-CINNAMIC ACID *v.* CINNAMIC ACID.

CARBOXY-CORNICULARIC ACID $C_{18}H_{14}O_5$ *i.e.* $C_6H_5.C(CO_2H):CH.CO.CH(CO_2H).C_6H_5$. Formed as a by-product in the reduction of pulvic acid to dihydrocornicularic-acid. It was not isolated, but was converted into the lactone by means of acetic anhydride.

Carboxy-cornicularic-lactone

$$C_{18}H_{12}O_4 \text{ or } \begin{array}{c} OC\text{——}O\quad CO_2H \\ |\qquad\quad |\qquad | \\ C_6H_5.C:CH.C : C.C_6H_5 \end{array} \quad [215°].$$

Long felted needles or short prisms. In cold aqueous NH_3 or alkaline carbonates it dissolves forming salts of the formula $C_{18}H_{11}O_4M$, but on heating it gives salts of carboxy-cornicularic acid $C_{18}H_{12}O_5M_2$ (Spiegel, *B.* 15, 1546).

CARBOXY-CYANAMIDO-BENZOYL *v.* p. 155.

DI-CARBOXY-GLUTACONIC ACID $C_7H_6O_8$. *Propylene tetracarboxylic acid.*

Ethyl ether $(CO_2Et)_2.CH.CH:C(CO_2Et)_2$. (270°-280°). S.G. 1·131 at 15°. From its sodium salt by HCl. Oil, soluble in alcohol or ether. Boiled with HCl it gives off CO_2 and forms glutaconic acid (*q. v.*) and iso-aconitic ether. NaOH acts similarly. *Sodium derivative* $(CO_2Et)_2.CNa.CH:C(CO_2Et)_2$. [260°]. From malonic ether, NaOEt and chloroform (Conrad a. Guthzeit, *A.* 222, 251): $2(CO_2Et)CNa_2 + CHCl_3 = (CO_2Et)_2.CNa.CH:C(CO_2Et)_2 + 3NaCl$. Bright yellow prisms. Insol. ether, sl. sol. cold water or cold alcohol, v. sol. hot water or hot alcohol. Gives a violet colour with ferric chloride, and pps. with metallic salts. Sodium amalgam reduces it to *dicarboxy-glutaric acid*, $(CO_2H)_2CH.CH_2.CH(CO_2H)_2$ [167°]. When this acid is heated it gives off CO_2, becoming glutaric acid.

Methyl di-carboxy-glutaconic ether.—Sodium di-carboxy-glutaconic ether heated with alcoholic MeI at 150° forms methyl-di-carboxy-glutaconic ether, $(CO_2Et)_2.CMe.CH:C(CO_2Et)_2$, an oil, which on saponification gives rise to $(CO_2H)_2CMe.CH:C(CO_2H)_2$, and this readily splits off CO_2, forming *methyl-glutaconic acid*, $CO_2H.CHMe.CH:CH.CO_2H$ [137°]. Methyl glutaconic acid forms white crystals; v. sol. water, alcohol, or ether.

Benzyl-di-carboxy-glutaconic ether $(CO_2Et)_2.C(C_7H_7).CH:C(CO_2Et)_2$, [78°], is formed in a similar way, using benzyl chloride. Insol. water, v. sol. hot alcohol, ether, or conc. H_2SO_4. When saponified by caustic soda it gives off CO_2 carbonic acid and forms *benzyl-glutaconic acid* $CO_2H.CH(C_7H_7).CH:CH.CO_2H$, [145°].

DI-CARBOXY-GLUTARIC ACID *v.* DI-CARBOXY-GLUTACONIC ACID.

CARBOXYL. *Oxatyl.* The monovalent acid radicle CO_2H *i.e.* CO.OH. Its hydrogen is always displaceable by metals, *cf.* ACIDS.

CARBOXYLIC ACID, so-called, *v.* DI-OXY-BENZENE-DI-QUINONE.

Di-hydro-carboxylic acid *v.* TETRA-OXY-QUINONE.

Tri-hydro-carboxylic acid *v.* HEXA-OXY-BENZENE.

Oxy-carboxylic acid *v.* BENZENE TRI-QUINONE.

v-**CARBOXY-OXAMIC ACID** *Di-ethyl ether.* $C_7H_{11}NO_5$ *i.e.* $CO_2Et.NH.CO.CO_2Et$. [45°]. From $ClCO.CO_2Et$ and oxamic ether (Saloman, *J. pr.* [2] 9, 292). Needles (from ether); sol. water and alcohol.

o-**CARBOXY-PHENOXY-ACETIC ACID** $C_6H_4(CO_2H).O.CH_2.CO_2H$. *Carboxy-phenyl-glycollic acid.* [187°]. Formed by oxidation of *o*-aldehydo-phenoxy-acetic acid with $KMnO_4$. White needles. Sol. alcohol, ether, and hot water.—$A''Ag_2$: white, sparingly soluble pp.

Di-ethyl ether $A''Et_2$: liquid.

Di-amide $C_7H_6O(CO.NH_2)_2$. [158°]. Long yellow needles, sparingly soluble in ether, benzene, and hot water, v. sol. chloroform and hot alcohol (Rossing, *B.* 17, 2995).

m-**Carboxy-phenoxy-acetic acid** $C_6H_4(CO_2H).O.CH_2.CO_2H$ [1:3]. [206°]. Prepared by oxidation of *m*-aldehydo-phenoxy-acetic acid with $KMnO_4$. Needles; v. sol. alcohol, ether, and acetic acid, sl. sol. cold water.—$A''Ag_2$: crystalline (Elkan, *B.* 19, 3044).

p-**Carboxy-phenoxy-acetic acid** $C_6H_4(CO_2H).O.CH_2.CO_2H$ [1:4]. [278°]. Prepared by oxidation of *p*-aldehydo-phenoxy-acetic acid with $KMnO_4$. White needles; v. sol. alcohol, ether, and acetic acid, more sparingly in benzene, chloroform, and ligroïn, sl. sol. cold water.

Salts.—$A''Ag_2$: white sparingly soluble pp. The Pb, Cu, and Fe salts are sparingly soluble pps. The Cu and Ba salts are soluble (Elkan, *B.* 19, 3044).

o-**CARBOXY-PHENYL-ACETIC ACID** $C_6H_4(CO_2H)CH_2.CO_2H$ [1:2]. *Homophthalic acid, Phenyl-acetic-carboxylic acid. Isuvitic acid.* [174°]. Formed by saponification of benzyl-cyanide-*o*-carboxylic acid by boiling with dilute KOH. Colourless crystals. V. sol. alcohol and hot water, insol. benzene.

Salts.—$A''Ag_2$: insoluble amorphous pp.—$A''Ca\,2aq$: sparingly soluble crystalline powder.—$A''Ba$: easily soluble crystals (Wislicenus, *B.* 18, 173).

Anhydride $C_6H_4\begin{cases}CH_2.CO \\ \quad\;\;\; | \\ CO-O\end{cases}$. [141°]; long prisms; v. sol. ether and chloroform. Formed by the action of acetyl chloride on the acid.

Ethyl ether $A''Et_2$: (292°); thick aromatic oil (Gabriel, *B.* 20, 2499).

Imide $C_6H_4\begin{cases}CH_2.CO \\ \quad\;\;\; | \\ CO.NH\end{cases}$ (di-oxy-isoquinoline): [c. 233°]. Formed by dry distillation of the ammonium-salt. Short colourless needles (from alcohol or acetic acid). Sublimes in long crystals. Sl. sol. alcohol. Dissolves in aqueous caustic alkalis. Heated with $POCl_3$ at 150°–

170° it is converted into di-chloro-iso-quinoline.

Methyl-imide $C_6H_4<\begin{matrix}CH_2.CO\\ | \\ CO.NMe\end{matrix}$: [123°]; (314°–318°); long colourless needles; v. sol. ordinary solvents. Dissolves in aqueous alkalis. Obtained by dry distillation of the methylamine salt of the acid. By MeI and methyl-alcoholic KOH at 100° it is converted into a tri-methyl derivative $C_6H_4<\begin{matrix}CMe_2.CO\\ | \\ CO.NMe\end{matrix}$, [103°], which is also obtained by methylation of the imide (Gabriel, *B.* 19, 1654, 2354, 2363). The *imide* and *methylimide* combine with diazo-benzene in alkaline solution.

Amic acid $C_6H_4(CO_2H).CH_2.CONH_2$ (homo-phthalamic acid): [187°]; colourless needles. Formed by slowly warming benzyl-cyanide-*o*-carboxylic acid $C_6H_4(CO_2H).CH_2.CN$ with conc. H_2SO_4 to 70°, and pouring into water.

Amic methyl ether $C_6H_4(CO_2Me).CH_2.CONH_2$: [112°]; crystalline solid (Gabriel, *B.* 20, 1203).

Benzene-azo-carboxy-phenyl-acetic-imide $C_6H_4<\begin{matrix}CH-N_2-C_6H_5\\ \\ CO.NH.CO\end{matrix}$. [260°]. Formed by the action of diazo-benzene chloride upon an alkaline solution of the imide of carboxy-phenyl-acetic acid. Orange-yellow needles (Gabriel, *B.* 20, 1205).

CARBOXY-PHENYL-BENZ-GLYCOCYAMIDINE *v.* BENZGLYCOCYAMIDINE.

CARBOXY-PHENYL-GLYCOLLIC ACID *v.* CARBOXY-PHENOXY-ACETIC ACID.

CARBOXY-PHENYL-MALONAMIC ACID.

Ethyl ether $CO_2Et.CH_2.CO.NH.C_6H_4.CO_2H$. [173°]. A product of the action of malonic ether on *m*-amido-benzoic acid (Schiff, *A.* 232, 144; *B.* 17, 403). Silvery needles. When heated it breaks up into malonic ether and malonyl-di-amido-di-benzoic acid:

$$2CO_2Et.CH_2.CO.NH.C_6H_4.CO_2H = CO_2Et.CH_2.CO_2Et + CH_2(CONH.C_6H_4.CO_2H)_2.$$

***o*-CARBOXY-PHENYL-METHYL-ACETIC ACID** $C_6H_4(CO_2H).CHMe.CO_2H$. *a-Methyl-homo-o-phthalic acid. Hydratropic-o-carboxylic acid.* [147°]. Formed by heating the imide with fuming HCl at 200°. Colourless crystalline powder.—$A''Ag_2$: crystalline pp.

Imide $C_6H_4<\begin{matrix}CHMe.CO\\ \quad | \\ CO \quad NH\end{matrix}$. *Di-oxy-methyl-isoquinoline.* [145°]. Formed by heating *o*-cyano-phenyl-methyl-aceto-nitrile $C_6H_4(CN).CHMe.CN$ with conc. H_2SO_4 at c. 130° and pouring into water. Glistening prisms. Can be distilled undecomposed. Dissolves in aqueous alkalis. By digestion with alcoholic KOH and MeI it is converted into the methyl-imide of carboxy-phenyl-di-methyl-acetic acid $C_6H_4<\begin{matrix}CMe_2.CO\\ | \\ CO.NMe\end{matrix}$. By $POCl_3$ it is converted into (*Py.* 2:4:1)-di-chloro-methyl-isoquinoline, whilst (*Py.* 4:2:1)-chloro-oxy-methyl-isoquinoline is formed as a by-product (Gabriel, *B.* 20, 2503).

***o*-Carboxy-phenyl-di-methyl-acetic acid** $C_6H_4(CO_2H).CMe_2.CO_2H$. *Di-methyl-homo-o-phthalic acid.* [c. 123°]. Obtained by dissolving the anhydride in boiling aqueous NaOH and ppg. with HCl. On heating it is reconverted into the anhydride. By distillation with soda lime it gives isopropyl-benzene.—$A''Ag_2$: crystalline pp.—$A''K_2aq$: plates.

Anhydride $C_6H_4<\begin{matrix}CMe_2-CO\\ \quad | \\ CO-O\end{matrix}$. [85°]. (312°) at 760 mm. Prepared by heating the imide or methylimide with fuming HCl (4 pts.) at 210° for 4 or 5 hrs. Flat crystals, slowly dissolved by aqueous alkalis, forming salts of the acid.

Imide $C_6H_4<\begin{matrix}CMe_2-CO\\ \quad | \\ CO-NH\end{matrix}$ (di-methyl-homo-phthalimide): [120°]; (318°) at 770 mm. Prepared by the action of methyl iodide on a solution of the imide of carboxy-phenyl-acetic acid in methyl-alcoholic KOH at 100°. Flat needles.

Methyl-imide $C_6H_4<\begin{matrix}CMe_2.CO\\ | \\ CO-NMe\end{matrix}$ (tri-methyl-homo-phthalimide). [103°]. (295°) at 770 mm. Formed by further methylation of the preceding imide or of the methylimide of *o*-carboxy-phenyl-acetic acid $C_6H_4<\begin{matrix}CH_2.CO\\ | \\ CO.NMe\end{matrix}$. Long needles. Slowly sublimes at 100°. V. sol. ordinary solvents, insol. alkalis (Gabriel, *B.* 19, 2363; 20, 1198).

CARBOXY-PHENYL-METHYL-*v*-*m*-PYRRYL-BENZOIC ACID $C_{19}H_{15}NO_4$ *i.e.* $\begin{matrix}HO_2C.C:CMe\\ | \\ HC:CPh\end{matrix}>N.C_6H_4.CO_2H$ [210°]. Obtained by saponification of its mono-ethyl-ether which is obtained by several days' standing of an acetic acid solution of acetophenone-aceto-acetic ether (1 mol.) and *m*-amido-benzoic acid (1 mol.). Aggregates of colourless needles. Sol. ordinary solvents except water.

Ethyl ether $\begin{matrix}EtO_2C.C:CMe\\ | \\ HC:CPh\end{matrix}>N.C_6H_4.CO_2H$: [160°]; slender yellow needles (from dilute acetic acid); sol. alcohol, ether, &c. Its Ca, Ba, Sr, and Mg salts are white granular pps. (Paal a. Schneider, *B.* 19, 3162).

***o*-CARBOXY-PHENYL OXAMIC ACID** $C_9H_7NO_5$ *i.e.* $C_6H_4(CO_2H).NH.CO.CO_2H$. [210°]. S. 11 at 10°.

Formation.—1. By heating oxalic acid with *o*-amido-benzoic acid at 120°.—2. From carbostyril and alkaline $KMnO_4$ (Friedländer a. Ostermaier, *B.* 14, 1916; 15, 334).—3. From acetyl-quinoline tetrahydride and cold dilute $KMnO_4$ (Hofmann a. König, *B.* 16, 734).—4. From cynurin or cynurenic acid and alkaline $KMnO_4$ (Kretschy, *M.* 4, 156; 5, 16).—5. Formed by oxidation of (*Py.*)-bromo-quinoline with $KMnO_4$ (Claus a. Collischonn, *B.* 19, 2767).

Properties.—Silvery needles (containing aq). (from water), or geodes (from ether). Decomposed by dilute acids, or by long boiling, into oxalic and amido-benzoic acids.

Salts.—$(NH_4)_2A''$: minute felted needles.—$KHA''\frac{1}{2}aq$.—$BaA''aq$.—$BaH_2A''_2aq$.—$CaA''2\frac{1}{2}aq$. $CuA''CuO\ 4aq$.—Ag_2A''.

Mono-ethyl ether
$C_6H_4(CO_2H).NH.CO.CO_2Et$. *Ethyl-oxalyl-anthranilic acid.* [181°]. Felted needles. Formed by oxidation of indoxylic ether or indoxanthic ether with CrO_3 (Baeyer, *B.* 15, 777).

m-**Carboxy-phenyl-oxamic acid**
$CO_2H.CO.NH.C_6H_4.CO_2H$. *Oxaloxyl-amido-benzoic acid.*

Formation.—1. By boiling an aqueous solution of the barium salt of cyano-carbimido-amido-benzoic acid.—2. By heating (equal mols. of) *m*-amido-benzoic acid and anhydrous oxalic acid for an hour at 180° (Griess, *B.* 16, 336; 18, 2412).

Properties.—Small white plates. V. sol. hot water, m. sol. alcohol, insol. ether.—BaA″ 2aq.

Mono-ethyl ether
$CO_2Et.CO.NH.C_6H_4.CO_2H$ (ethoxal-benzamic acid) [225°]. Formed by boiling *m*-amido-benzoic acid with oxalic ether (Schiff, *A.* 232, 132; *B.* 17, 402; *G.* 15, 534). Silky needles (from water or alcohol). When heated above 225° it splits up into oxalic ether and carboxy-phenyl-oxamide. *Amide-ether* $CO_2Et.CO.NH.C_6H_4.CONH_2$. [191·5°]. Got by heating *m*-amido-benzamide with oxalic ether. Gives with aniline the amide-anilide $CO(NHPh)CO.NH.C_6H_4CO.NH_2$ [c. 310°]. *Anilide-ether* $CO_2Et.CO.NH.C_6H_4.CONPhH$ [180°]. From *m*-amido-benzanilide and oxalic ether. Satiny needles.

Amic acid $CO(NH_2)CO.NH.C_6H_4.CO_2H$ *v.* PHENYL-OXAMIDE CARBOXYLIC ACID.

CARBOXY-PHENYL-OXAMIDE *v.* PHENYL-OXAMIDE CARBOXYLIC ACID.

CARBOXY-PHENYL-OXY-ACETIC ACID *v.* CARBOXY-PHENOXY-ACETIC ACID.

o-**CARBOXY-PHENYL PHENYL-CARBAMATE** $C_6H_4(CO_2H).O.CO.NHC_6H_5$.

Methyl ether $C_6H_4(CO_2Me).O.CO.NHC_6H_5$. [238°]; long needles; sublimable. Formed by heating methyl salicylate with phenylcyanate (Snape, *B.* 18, 2431).

m-**CARBOXY-PHENYL-PHOSPHORIC ACID** $C_6H_4(CO_2H).O.PO(OH)_2$ [201°]. From its chloride and water. Scales, v. sol. water, alcohol, and ether. Water at 160° decomposes it into phosphoric and *m*-oxy-benzoic acid (Anschütz a. Moore, *A.* 239, 333).

Chloride $C_7H_4Cl_3PO_3$ *i.e.* $C_6H_4(COCl).O.PO.Cl_2$. (170°) at 12mm. S.G. $\frac{20}{4}$ 1·548. From *m*-oxy-benzoic acid (1 mol.) and PCl_5 (1½ mols.). Further treatment with PCl_5 (1 mol.) produces $C_7H_4Cl_5PO_2$ (178°) at 11 mm. This is probably $C_6H_4(CCl_3).O.PCl_2$ and is converted by water into $C_6H_4(CO_2H).O.PO(OH)_2$. A further quantity of PCl_5 converts $C_7H_4Cl_5PO_2$ into $C_6H_4Cl.CCl_3$.

o-**CARBOXY-β-PHENYL-PROPIONIC ACID** $HO_2C.C_6H_4.CH_2.CH_2.CO_2H$. [166°]. Formed by heating *o*-carboxy-benzyl-malonic acid to 190° (Wislicenus, *A.* 242, 39, *cf.* Gabriel a. Michael, *B.* 10, 2204). Prisms, v. sol. hot, sl sol. cold, water.

CARBOXY-PHENYL-SEBACAMIC ACID $CO_2H.C_8H_{16}.CO.NH.C_6H_4.CO_2H$. [193°]. From its ether by saponification. Prisms.

Mono-ethyl ether
$CO_2Et.C_8H_{16}.CO.NH.C_6H_4.CO_2H$. [146°]. From sebacic ether and *m*-amido-benzoic acid (Pellizzari, *A.* 232, 146; *B.* 18, 215; *G.* 15, 550).

m-**CARBOXY-PHENYL-SUCCINAMIC ACID** $C_2H_4(CO_2H)CO.NH.C_6H_4.CO_2H$. *Benzamsuccinic acid.* [223°]. Colourless prisms. Its ethyl-ether is formed, together with di-phenyl-succinamide dicarboxylic acid, by boiling amido-benzoic acid with an alcoholic solution of succinic ether. On heating to its melting-point it loses H_2O and is converted into succinyl-amido-benzoic acid $C_2H_4<\substack{CO\\CO}>N.C_6H_4.CO_2H$ [235°].

Ethyl ether
$C_2H_4(CO_2Et)CO.NH.C_6H_4.CO_2H$ [174°]; glistening plates from water.

Amide $C_2H_4(CONH_2)CO.NH.C_6H_4.CO_2H$ [229°].

Anilide $C_2H_4(CONHPh)CO.NH.C_6H_4.CO_2H$ [252°] (Pellizzari, *A.* 232, 146; *B.* 18, 214; *G.* 15, 550; Muretoff, *J. R.* 4, 298).

p-**Carboxy-phenyl-succinamic acid** [4:1] $C_6H_4(CO_2H).NH.CO.CH_2.CH_2.CO_2H$. [226°]. From *p*-tolyl-succinimide and dilute aqueous $KMnO_4$ (Michael, *B.* 10, 577). Needles, sl. sol. cold water and cold alcohol. Boiling conc. HClAq gives succinic and *p*-amido-benzoic acids.—AgHA″.

o-**CARBOXY-PHENYL-SULPHURIC ACID** $CO_2H.C_6H_4.O.SO_2.OH$. *Salicyl-sulphuric acid.* Prepared by the action of $K_2S_2O_7$ on a solution of salicylic acid in strong KOH. By heating the K salt to 190° it gives K_2SO_4 and salicylide.—A″K_2. Colourless spikes. Readily decomposed by dilute acids into salicylic acid and $KHSO_4$ (Baumann, *B.* 11, 1914).

m-**Carboxy-phenyl-sulphuric acid** [3:1] $CO_2H.C_6H_4.O.SO_2.OH$. Prepared by the action of $K_2S_2O_7$ on a solution of *m*-oxybenzoic acid in strong KOH.—A″K_2: [220°–225° with decomposition]; needles, more stable towards dilute acids than the *ortho-* compound; is decomposed however at 100°.

p-**Carboxy-phenyl-sulphuric acid** [4:1] $CO_2H.C_6H_4.O.SO_2.OH$. Prepared by the action of $K_2S_2O_7$ on a solution of *p*-oxybenzoic acid in strong KOH.—A″K_2: leaflets or tables. Does not decompose till heated to 250°.

CARBOXY-PROPYL-ACETIC ACID *v.* ETHYL-SUCCINIC ACID.

CARBOXY-PYRRYL-GLYOXYLIC ACID $C_4NH_3(CO_2H).CO.CO_2H$. Formed by the oxidation of pyrrylene-di-methyl-di-ketone $(CH_3.CO)_2C_4H_2NH$, or of pyrryl-methyl-ketone carboxylic acid, with alkaline $KMnO_4$. Crystalline; sol. ether, alcohol, and boiling water, insol. benzene.—A″Ag_2: yellow pp.

Di-methyl ether A″Me_2: [145°]; long colourless needles; m. sol. hot alcohol, sl. sol. ether and benzene. Potash-fusion gives pyrrol di-carboxylic acid (Ciamician a. Silber, *B.* 19, 1412, 1957; *G.* 16, 373, 379).

CARBOXY-TARTRONIC ACID *v.* DI-OXY-TARTARIC ACID.

CARBYLO-DIACETONAMINE *v.* p. 27.

CARBYLAMINES *v.* CARBAMINES.

CARDAMOMS, OIL OF. Employed in medicine as a carminative.

1. *From Ceylon.* The seeds of *Elettaria major* contain 3·5 p.c. of an essential oil which consists of a terpene (170°–178°), terpinene, a solid substance [61°], and terpineol $C_{10}H_{18}O$ (205°–220°). The latter is converted by HCl into di-pentene hydrochloride, $C_{10}H_{16}2HCl$ [52°

and by HI into $C_{10}H_{16}2HI$ [76°]. The terpene also gives a hydrochloride $C_{10}H_{16}2HCl$ [52°]. A solid tetrabromide could not be got (Weber, *A.* 238, 98).

2. *From Malabar.* The oil from *Elettaria Cardamomum* slowly deposits crystals of $C_{10}H_{16}3H_2O$ (Dumas a. Péligot, *A. Ch.* [2] 57, 334).

CARDOL $C_{21}H_{30}O_2$ (?) An oil, occurring with anacardic acid (*q. v.*), in the pericarp of the cashew nut (*Anacardium occidentale*). It is sol. alcohol and ether. It is not volatile; it blisters the skin. It gives, with basic lead acetate a pp. of $C_{21}H_{29}(PbAc)O_2PbO$ (Städeler, *A.* 63, 137). Anacardic acid $C_{21}H_{30}(OH)CO_2H$ in alcoholic solution gives with metallic solutions pps. of the salts: AgA'. — CaA'2aq. — BaA'aq.—MgA'aq.—Its *methyl ether* is an oil (Ruhemann a. Skinner, *C. J.* 51, 663; *B.* 20, 1861).

CARICIN. An oily substance present in the seeds of the Papaw tree (*Carica papaya*) (Peckolt, *Ph.* [3] 10, 343).

CARMINAPHE *v.* NAPHTHOQUINONE.

CARMINIC ACID $C_{17}H_{18}O_{10}$. The colouring matter of cochineal which is obtained from insects of the genus *Coccus*, chiefly *Coccus cacti*. Cochineal contains only 10 p.c. colouring matter (Pelletier a. Caventou, *A. Ch.* [2] 7, 90; 8, 255; Warren de la Rue, *A.* 64, 1, 23; Schützenberger, *A. Ch.* [3] 54, 52; Schaller, *Bl.* [2] 2, 414; Méne, *C. R.* 68, 666; Dieterich, *C. C.* 1867, 287; Liebermann, *B.* 18, 1969). The lead salt is ppd. on adding lead acetate to an aqueous infusion of cochineal; by this means the quantity of colouring matter in cochineal may be estimated. Carmine, a red pigment prepared from cochineal, appears to be a compound of carminic acid with alumina, lime, and some organic acid. Cochineal also contains a fat (in which are ethers of myristic acid, of $C_{14}H_{28}O_2$ and of $C_{12}H_{22}O_2$ and a waxy substance, coccerin (Raimann, *M.* 6, 891; Liebermann, *B.* 19, 328).

Properties.—Purple mass, sol. water and alcohol, sl. sol. ether. Its solution forms red pps. with the alkaline earths and with acetates of Pb, Zn, Cu, and Ag. Alum and Na_2CO_3 give the aluminium lake.

Reactions.—1. Boiling dilute H_2SO_4 forms 'carmine-red' and a sugar $C_6H_{12}O_6$ (Hlasiwetz a. Grabowski, *A.* 141, 329). According to Liebermann the formation of sugar is questionable.—2. *Potash-fusion* gives coccinin, oxalic acid, and succinic acid (H. a. G.).—3. Conc. H_2SO_4 at 130° forms a compound $C_{32}H_{20}O_{13}$ and ruficoccin $C_{16}H_{10}O_6$ (Liebermann a. Dorp, *A.* 163, 105).—4. HNO_3 forms *nitro-coccic acid* $C_8H_5(NO_2)_3O_3$.—5. By distillation with *zinc-dust* a small quantity of a solid hydrocarbon $C_{16}H_{12}$ is produced, this forms plates melting at [187°] (Furth, *B.* 16, 2169).

Salts.—Na_2A''.—$K_2A''xaq$.—$BaA''xaq$.

Coccinin $C_{14}H_{12}O_5$. Prepared as above. Yellow laminæ (from alcohol); insol. water, v. sol. alcohol, sl. sol. ether. Sol. alkalis. The alkaline solutions are yellow and absorb oxygen, becoming green and, finally, purple. The solution in conc. H_2SO_4 turns indigo-blue on warming. On distillation with zinc-dust it yields a small quantity of a hydrocarbon $C_{14}H_{12}$ which forms plates melting at [187°].—$C_{14}H_{11}(NH_4)O_5$.

Acetyl derivative. Yellow crystals, sol alcohol and acetic acid, insol. water (Furth, *B.* 16, 2169).

Ruficoccin $C_{16}H_{10}O_6$. Formed as above. Brick-red powder, sl. sol. warm water and ether, m. sol. alcohol. The ethereal solutions fluoresce green. The alkaline solutions are brown. Conc. H_2SO_4 forms a violet solution.—$CaC_{16}H_8O_6$.

Compound $C_{32}H_{20}O_{13}$. Black insoluble powder. Forms violet solutions in KOHAq and conc. H_2SO_4. Both this compound and ruficoccin give $C_{16}H_{12}$ [187°] when distilled over zinc-dust.

Carmine red $C_{11}H_{12}O_7$. Formed by boiling carminic acid with dilute H_2SO_4 (*v. supra*). Dark purple mass with green lustre; scarlet when powdered. Alcohol and water form red solutions. Insol. ether. Potash-fusion forms coccinin. Water at 200° forms ruficarmine $C_{16}H_{12}O_6$.—**Salts:** $K_2C_{11}H_{10}O_7$. $CaC_{11}H_{10}O_7xaq$ — $BaC_{11}H_{10}O_7xaq$. — $ZnC_{11}H_{10}O_7xaq$. — $Zn(C_{11}H_{11}O_7)_2xaq$.

If carmine-red be dissolved in acetic acid, and treated with bromine two products are obtained, named provisionally (*a*)- and (*β*)-*bromo-carmine*. The (*a*)-bromo-carmine is sparingly soluble in acetic acid and separates in crystals (yield: 10 p.c.), whilst the amorphous (*β*)-bromo-carmine remains in solution and is ppd. on adding water (the yield is 20 p.c.).

'(*a*)-Bromo-carmine' $C_{10}H_4Br_4O_3$ crystallises in colourless needles, [248°], v. sol. alkalis. By boiling with strong aqueous KOH it gives

'(*a*)-Bromo-dioxy-carmine,' so called, $C_{10}H_6Br_2O_5$, which forms colourless crystals, [208°]. By its behaviour on etherification it is shown to contain one CO_2H and one phenolic OH group. On oxidation with $KMnO_4$ it yields two bodies:—(*a*) An acid $C_9H_6Br_2O_4$ which forms colourless crystals [211°]. By its reactions on methylation it is proved to contain one OH and CO_2H group, whence it probably has the constitution $C_6(CH_3)Br_2(OH)(CHO)CO_2H$ or $C_6H(CH_3)Br_2(OH)CO.CO_2H$. (*b*) A neutral body $C_9H_4Br_2O_4$, [195°], which by its reactions is shown to be a di-bromo-oxy-methyl-phthalic anhydride $C_6MeBr_2(OH)C_2O_2$:O [1:2:4:3:5:6].

'(*β*)-Bromo-carmine,' so called, is the second product of the bromination of carmine-red, and separates in yellow amorphous flocks on adding water to the acetic acid solution. It is v. sol. alcohol, acetic acid, &c., but could not be obtained in a pure state. By boiling with strong aqueous KOH it is converted into

'(*β*)-Bromo-oxy-carmine' $C_{11}H_7Br_3O_4$, which forms glistening yellow needles, [232°]. It is a di-basic acid and forms red salts. On oxidation with $KMnO_4$ it yields two bodies:—(*a*) An acid $C_{10}H_8Br_2O_6$ which forms colourless prisms (containing aq), and melts at [230°] with evolution of CO_2. From its reactions it probably has the constitution $C_6MeBr_2(OH)(CO_2H)CO.CO_2H$. (*b*) A neutral body $C_9H_4Br_2O_4$ identical with that obtained from the '(*a*)-bromo-oxy-carmine' (Will a. Leymann, *B.* 18, 3180).

CARMUFELLIC ACID $C_{12}H_{20}O_{16}$. An acid said to be formed by the action of HNO_3 on the aqueous extract of cloves. Micaceous scales.

insol. alcohol, ether, and cold water (Muspratt a. Danson, *P. M.* [4] 2, 293).

CARNAÜBA WAX. Obtained from the leaves of *Copernicia cerifera* in Brazil, and largely used there for making candles. It contains myricylic alcohol, $C_{29}H_{59}CH_2OH$ [85·5°], a hydrocarbon, [59°] and compound ethers derived from the following alcohols and acids: myricyl alcohol; an alcohol $C_{26}H_{53}CH_2OH$ [76°]; a di-hydric alcohol $C_{23}H_{46}(CH_2OH)_2$ [104°]; an isomeride of lignoceric acid, $C_{23}H_{47}CO_2H$ [72·5°]; an acid isomeric or identical with cerotic acid $C_{26}H_{53}CO_2H$ [79°]; and an oxy-acid of the formula $C_{19}H_{38}(CH_2OH)(CO_2H)$ or its lactone [103·5°]. The alcohol $C_{23}H_{46}(CH_2OH)_2$ gives on oxidation an acid $C_{23}H_{46}(CO_2H)_2$ [102·5°]; and the oxy-acid $C_{19}H_{38}(CH_2OH)(CO_2H)$ gives the acid $C_{19}H_{38}(CO_2H)_2$ [90°] (Stürcke, *A.* 223, 283; *cf.* Lewy, *A. Ch.* [3] 13, 438; Brandes, *T.* 1811, 261; Maskelyne, *C. J.* 22, 87; Bérard, *Z.* [2] 4, 415). The greater part of the wax is myricyl cerotate and myricyl alcohol.

CARNINE $C_7H_8N_4O_3$. A substance occurring in extract of meat, and in the product of boiling yeast with water (Weidel, *A.* 158, 353; Schützenberger, *C. R.* 78, 493). Obtained by boiling with water the pp. thrown down from meat extract by lead acetate; the carnine crystallises from the evaporated filtrate (Kruckenberg a. Wagner, *C. C.* 1884, 107). Crystallises with aq, v. sl. sol. cold water, insol. alcohol and ether. Bromine-water converts it into hypoxanthine $C_5H_4N_4O$.—B'HCl: needles.—$B'_2H_2PtCl_6$.

CARPENE C_9H_{14}. (156°). Obtained, together with *p*-cresol, by distilling calcium podocarpate. Oil, smelling of turpentine; resinifies in the air. Forms an oily compound with bromine (Oudemans, *B.* 6, 1125; *A.* 170, 252).

CARROTIN $C_{26}H_{38}$ (?) *Carrotene.* The colouring matter of the carrot (*Daucus Carota*) (Wackenroder, *Geiger's Mag.* 33, 144; Zeise, *J. pr.* 40, 297; Husemann, *A.* 117, 200). Occurs also as a normal constituent in the leaves of plants, and in the tomato (Arnaud, *C. R.* 102, 1119; 104, 1293; *Bl.* [2] 46, 487; 48, 64). Inasmuch as no other coloured hydrocarbon is known, carrotin probably contains oxygen.

Preparation.—The roots are cut up and pressed, dried at 80° and extracted with CS_2. The juice is ppd. with lead acetate and the pp. also extracted with CS_2. Carrotin, hydrocarrotin, and fat are obtained from the CS_2 solutions. The fat is saponified with alcoholic potash. Water and $BaCl_2$ are added. The pp. is dried and extracted with acetone. On recrystallising from methyl alcohol hydrocarrotin separates out first (Reinitzer, *M.* 7, 597).

Properties.—Small red plates, v. sol. CS_2, benzene; v. sl. sol. absolute alcohol; and less sol. 90 p.c. alcohol. Insol. Aq. Rapidly absorbs oxygen from the air. Dissolves in conc. H_2SO_4 giving a deep blue colour. Yields a derivative $C_{26}H_{38}I_2$ with iodine; this has a deep green colour, and metallic lustre. Chlorine forms a chloro-derivative [120°].

Hydrocarrotin $C_{26}H_{44}O$ (?). [138°]. $[\alpha]_D = -37·4°$ in $CHCl_3$ at $-3·4°$. Prepared as above. Greatly resembles cholesterin. Colourless, insol. water, v. sol. alcohol, acetone ether, $CHCl_3$ and CS_2. Crystallises from acetone in long needles, and from methyl alcohol in plates containing water. Resembles Liebermann's cholestol and Hesse's cupreol but differs from phytosterin (Reinitzer, *M.* 7, 597).

Acetyl derivative [128°]; coloured green by H_2SO_4, and rose by addition of chloroform.

Benzoyl derivative [145°].

CARTHAMIN $C_{14}H_{16}O_7$. The colouring matter of safflower (*Carthamus tinctorius*) (Chevreul; Schlieper, *A.* 58, 362). Washed safflower is treated with aqueous Na_2CO_3, acetic acid is added and pieces of cotton are put in. The carthamine that has been taken up by the cotton is subsequently dissolved off it by aqueous Na_2CO_3, and ppd. by citric acid. Powder with red lustre (from alcohol); sl. sol. water, insol. ether, v. sol. alcohol. Its alcoholic solution is purple. Decomposed by boiling with water or alkalis. Potash-fusion gives oxalic and *p*-oxybenzoic acids (Malin, *A.* 136, 117).

CARVACROL. $C_{10}H_{14}O$ *i.e.* $C_6H_3MePr(OH)$ [1:4:2]. *Cymenol.* Mol. w. 150. [c. 0°]. (237° i.V.). S.G. $\frac{15}{15}$ ·986. μ_D 1·5252. H.F. p. 68,181 $[(C,O_2) = 94,000; (H_2,O) = 69,000]$ (Stohmann, *J. pr.* [2] 34, 319). Occurs in the essential oil of *Origanum hirtum* and, together with cymene and a terpene, in oil of *Satureja hortensis* and *S. montana*; in oil of mint and of *Thymus Serpyllum* (Jahns, *Ar. Ph.* [3] 16, 277; *B.* 15, 816; Haller, *Bl.* [2] 37, 411; *C. R.* 94, 132; Beyer, *Ar. Ph.* [3] 21, 283).

Formation.—1. By boiling carvol (50 pts.) diluted with oil of caraway (50 pts.) with glacial phosphoric acid (12 pts.) for 3 or 4 hours (Lustig, *B.* 19, 11; *cf.* Völckel, *A.* 35, 308; 85, 246; Kekulé a. Fleischer, *B.* 6, 1088; Kreysler, *B.* 18, 1704).—2. From camphor (5 pts.) by boiling with iodine (1 pt.) (Kekulé a. Fleischer, *B.* 6, 934; *cf.* Claus, *J. pr.* 25, 264; Schweizer, *J. pr.* 26, 118; *A.* 40, 329).—3. From bromo-camphor and $ZnCl_2$ (Schiff, *B.* 13, 1408).—4. Pure camphor cymene is converted into its monosulphonic acid and the latter carefully fused with 3 pts. of KOH (Jacobsen, *B.* 11, 1060; *cf.* Pott, *B.* 2, 121; H. Müller, *B.* 2, 130).

Properties.—Oil. Fe_2Cl_6 colours its alcoholic solution green.

Reactions. — 1. On fusing with KOH isooxycuminic acid $C_6H_3(CO_2H)(OH)C_3H_7$ [1:2:4] is first formed and finally oxy-terephthalic acid is produced (*B.* 11, 1060).—2. P_2S_5 gives cymene and thio-carvacrol $C_{10}H_{14}S$.—3. P_2O_5 forms cresol and propylene.—4. Fe_2Cl_6 gives di-carvacrol.—5. PCl_5 forms chloro-cymene.—6. *Diazo-benzene* forms $C_6H_2MePr(OH).N_2.C_6H_5$ [80°–85°] and $C_6HMePr(OH)(N_2C_6H_5)_2$ [126°] (Mazzara, *G.* 15, 214).—7. *Chloro-acetic acid* in presence of an alkali forms carvacryl-glycollic acid $C_{10}H_{13}O.CH_2.CO_2H$.—8. H_2SO_4 forms one or two sulphonic acids of the form $C_6H_2MePr(OH).SO_3H$. According to Jahns one only is formed, its salts being: KA'aq.—AgA'2aq.—$BaA'_2$5aq. S. 12·5 at 15°.—$MgA'_2$12aq.

Sodium salt.—$C_{10}H_{13}ONa$: white crystalline powder.

Methyl ether $C_{10}H_{13}OMe$. (217°). S.G. $\frac{0}{}$ ·954 (Paterno a. Pisati, *B.* 8, 71; *G.* 5, 13). Forms with H_2SO_4 two acids $C_{10}H_{12}(SO_3H)(OMe)$ whose Ba salts are BaA'_2 $3\frac{1}{2}$aq: v. sl. sol. water, and $BaA'_2$5aq, v. sol. water.

Ethyl ether $C_{10}H_{13}OEt$: (235°); oil having

an odour of carrots (Lustig, *B.* 19, 11; *C. C.* 1884, 787).

Acetyl derivative $C_{10}H_{13}OAc$: (246°). S.G. $\frac{0}{0}$ 1·011; colourless liquid heavier than water.

Benzoyl derivative $C_{10}H_{13}OBz$: (above 260°); thick odourless oil.

Dicarvacrol. $C_{20}H_{26}O_2$. [154°]. Formed by the action of neutral Fe_2Cl_6 on carvacrol (Dianin, *J. R.* 14, 141). Thin silky needles (from dilute alcohol); insol. water, v. sol. alcohol and ether.

o-**CARVACROTIC ACID** $C_{10}H_{12}(OH)CO_2H$. *Oxy-cymene-carboxylic acid.* [136°]. Prepared by passing CO_2 over heated sodium carvacrol. White silky needles. Sublimable. V. sol. hot water, alcohol, and ether, nearly insol. cold water. Alcoholic Fe_2Cl_6 gives a violet colouration (Lustig, *B.* 19, 18).

p-**Carvacrotic acid** $C_{10}H_{12}(OH)CO_2H$. *Oxy-cymene-carboxylic acid.* [80°]. Obtained by oxidation of carvacrotic aldehyde (from carvacrol, $CHCl_3$, and NaOH) with $KMnO_4$. Long white silky needles. Can be sublimed and distilled with steam. V. sol. hot water, alcohol, and ether, nearly insol. cold water. Green colouration with alcoholic Fe_2Cl_6 (Lustig, *B.* 19, 16).

p-**CARVACROTIC ALDEHYDE**

$C_6H_2(CH_3)(C_3H_7)(OH)(CHO)$ [1:4:2:5] (?) *Oxy-aldehydo-cymene.* (c. 236°). Formed by heating carvacrol with aqueous NaOH and chloroform. Oil. Volatile with steam (Lustig, *B.* 19, 14).

An isomeride [96°] has also been described as *p*-carvacrotic aldehyde. It is left as a residue after distilling off the volatile aldehyde with steam. White silky flat plates. Easily soluble in alcohol, ether, and benzene, sparingly in hot water, insoluble in cold water (Nordmann, *B.* 17, 2632).

CARVACRYL-AMINE $C_{10}H_{13}NH_2$. *Methyl-propyl-phenyl-amine.* (242°). Formed, together with di-carvacryl-amine, by heating carvacrol with ammoniacal $ZnBr_2$ or $ZnCl_2$ and NH_4Br or NH_4Cl at 350°–360°; yield, 25 to 30 p.c. Colourless oil, which solidifies at −16° $B'_2H_2Cl_2PtCl_4$: yellow prisms, sl. sol. hot water.

Acetyl derivative $C_{10}H_{13}NHAc$: [115°]; white glistening tables; sl. sol. hot water, v. sol. warm alcohol.

Benzoyl derivative $C_{10}H_{13}NHBz$: [102°]; flat glistening crystals; nearly insol. water, sl. sol. cold alcohol, v. sol. hot alcohol, and benzene (Lloyd, *B.* 20, 1261).

Di-carvacryl-amine $(C_{10}H_{13})_2NH$. (344°–348°). Formed as above, the yield is 27 to 40 p.c. Colourless oil. V. sol. alcohol, ether, and benzene. Its solution in conc. H_2SO_4 is coloured blue by nitrites and nitrates.—B'HCl.—$B'_2H_2Cl_2PtCl_4$.

Acetyl derivative $(C_{10}H_{13})_2NAc$: [78°]; white glistening scales; v. sol. hot alcohol and ligroïn, sl. sol. in the cold (Lloyd, *B.* 20, 1261).

CARVACRYL-GLYCOLLIC ACID $C_{12}H_{16}O_3$ *i.e.* $C_{10}H_{13}O.CH_2.CO_2H$. [140°]. From carvacrol, chloro-acetic acid and potash (Spica, *G.* 10, 345). Flat needles.—PbA'.—AgA'.

Ethyl ether EtA'. [c. 100°]. (289°).

Amide $C_{12}H_{15}O_2.NH_2$. [68°].

CARVACRYL-LACTIC ACID $C_{13}H_{18}O_3$ *i.e.* $C_{10}H_{13}O.CMeH.CO_2H$. [74°]. From carvacrol, α-chloro-propionic acid, and potash (Scichilone, *G.* 12, 49). Prisms, v. e. sol. alcohol, ether, and chloroform.

CARVACRYL MERCAPTAN $C_{10}H_{14}S$ *i.e.* $C_6H_3MePr(SH)$ [1:4:2]. (236°). S.G. $\frac{17.5}{}$ ·998. From camphor or carvacrol and P_2S_5 (Flesch, *B.* 6, 478; Roderburg, *B.* 6, 669; Kekulé a. Fleischer, *B.* 6, 934). Liquid. HNO_3 oxidises it to sulpho-toluic acid (Bechler, *J. pr.* [2] 8, 168).

Salts.—$Hg(C_{10}H_{13}S)_2$. [109°] (Fittica, *A.* 172, 327). — $C_{10}H_{13}S.HgCl$. — $C_{10}H_{13}SAg$. — $C_{10}H_{13}SAgAgNO_3$.

Methyl ether $C_{10}H_{13}SMe$. (244°). S.G. ·99.

TRI-CARVACRYL PHOSPHATE

$PO(OC_{10}H_{13})_3$. [75°]. Colourless prisms or tables. Easily soluble in alcohol, ether, and benzene, more sparingly in petroleum-ether. Formed by heating carvacrol with $POCl_3$; yield, 55–60 p.c. of the theoretical (Kreysler, *B.* 18, 1704).

CARVACRYL-PHOSPHORIC ACID

$C_6H_3MePr.O.PO_3H_2$ [1:4:2]. Formed by the action of $POCl_3$ upon carvacrol, and treatment with aqueous K_2CO_3. The potassium salt A'K5aq forms large silvery plates. By alkaline $KMnO_4$ it is oxidised to oxyisopropyl-salicylic acid $C_6H_3(CMe_2OH)(OH)CO_2H$ [4:2:1] (Heymann a. Königs, *B.* 19, 3309).

TETRA-CARVACRYL SILICATE $Si(OC_{10}H_{13})_4$. (380°–390°) at 118 mm. Colourless oil. Formed by heating carvacrol with $SiCl_4$; the yield is 85 p.c. of the theoretical (Hertkorn, *B.* 18, 1694).

CARVACRYL-SULPHURIC ACID

$C_6H_3MePr.O.SO_3H$ [1:4:2]. *Cumyl-sulphuric acid.* The *potassium salt* is formed by adding potassium pyrosulphate to a warm solution of carvacrol in aqueous KOH. Silvery plates. V. sol. water and alcohol. By alkaline permanganate it is oxidised to oxyisopropyl-salicylic acid $C_6H_3(CMe_2OH)(OH)CO_2H$ [4:2:1] (Heymann a. Königs, *B.* 19, 3309).

CARVENE. A terpene present in oil of caraway, *v.* TERPENES.

Nitroso-carvene *v.* CARVOXIM.

CARVEOL $C_{10}H_{15}.OH$. (219°). Thick fluid. Formed by reduction of carvol with sodium and alcohol. With phenyl cyanate it reacts to form carveyl-phenyl-carbamate [84°] (Leuchart, *B.* 20, 114).

CARVEYL PHENYL-CARBAMATE

$C_{10}H_{15}O.CO.NPhH$. [84°]. Formed by the action of phenyl cyanate upon carveol $C_{10}H_{15}.OH$. Slender needles. V. sol. hot alcohol, sl. sol. ether and ligroïn (Leuchart, *B.* 20, 114).

CARVOL $C_{10}H_{14}O$. (228°) (R. Schiff, *B.* 19, 562). S.G. $\frac{15}{}$ ·9667 (Gladstone, *C. J.* 49, 621); $\frac{22.5}{}$ ·9574 (Flückiger, *Ar. Ph.* [3] 22, 361). μ_D 1·5020 (G.). R_∞ 76·68 (G.). S.V. 190·26. H.F.p. 48,250 ((C,O_2) = 94,000; (H_2,O) = 69,000) (Stohmann, *J. pr.* [2] 34, 322).

Occurrence.—In oil of caraway (*oleum carvi*) together with carvene (173°) (Völckel, *A.* 85, 246). In oil of dill (*Anethum graveolens*) and of mint (*Mentha crispa*). The carvol in the oils of caraway and of dill is dextro-rotatory, but that from oil of mint is lævo-rotatory $[\alpha]_D$ = −62·46 at 2° (Beyer, *Ar. Ph.* [3] 21, 283). According to Flückiger (*Ar. Ph.* [3] 22, 361) the rotatory power of carvol is $[\alpha]_D$ = 58·2°.

Properties.—Liquid. Carvol from all three sources forms the same crystalline compound $(C_{10}H_{14}O)_2H_2S$ [187°] when H_2S is passed into its alcoholic solution. When prepared from oils

of caraway or of dill this compound is dextro-rotatory, $[\alpha]_D = +5{\cdot}5°$ at 20°, but when obtained from oil of mint it is lævo-rotatory, $[\alpha]_D = -5{\cdot}5°$ at 20°. Dilute alcoholic KOH in the cold liberates carvol from this compound. Protracted treatment with H_2S converts carvol in alcoholic solution into the amorphous $(C_{10}H_{14}S)_2H_2S$.

Reactions.—1. Distillation over solid KOH or P_2O_5 changes carvol into the isomeric carvacrol (Kekulé a. Fleischer, *B.* 6, 1088).—2. P_2S_5 forms cymene. — 3. P_2S_5 gives thio-carvacrol $C_{10}H_{13}SH$.—4. Distillation over *heated zinc-dust* gives $C_{10}H_{16}$ (173°) and cymene (Arndt, *Z.* [2] 4, 730; *B.* 1, 204).—5. *Sodium* in alcohol forms carveol (*q. v.*).—6. Dry HCl gas passed into a mixture of carvol (1 mol.) and *aceto-acetic ether* (1 mol.) forms the compound $C_{16}H_{25}ClO_4$ possibly $C_9H_{15}Cl{:}C(OH).CH(CO.CH_3)CO_2Et$. [146°]. Glistening white prisms (Goldschmidt a. Kisser, *B.* 20, 489).—7. *Hydroxylamine* forms the oxim, *v.* CARVOXIM.

Carvol - phenyl - hydrazide $C_{10}H_{14}{:}N_2HC_6H_5$. [106°]. Formed by the action of phenyl-hydrazine on carvol (Goldschmidt, *B.* 17, 1578). Slender white needles. Sol. hot water.

Carvol-chloro-hydride $C_{10}H_{15}ClO$. *Hydrochlorocarvol.* Oil. Formed by leading dry HCl into carvol.

Oxim $C_{10}H_{15}Cl(NOH)$: [132°]; tables. Formed by the action of hydroxylamine upon carvol-chloro-hydride or of HCl upon carvoxim.

Benzoyl-oxim $C_{10}H_{15}Cl(NOBz)$: [115°]; needles (from petroleum-spirit) (Goldschmidt a. Zürrer, *B.* 18, 2220).

Phenyl - hydrazide $C_{10}H_{15}Cl(N_2HPh)$: [137°]; small white prisms.

Carvol bromo-hydride $C_{10}H_{15}BrO$. Oil. Decomposing at about 50°.

Oxim $C_{10}H_{15}Br(NOH)$: [116°]; prisms (from ligroïn).

Phenyl - hydrazide $C_{10}H_{15}Br(N_2HPh)$: [119°]; slender yellow needles (Goldschmidt a. Kisser, *B.* 20, 488, 2071).

Constitution of carvol.

```
         HC — CPr  = CH
Carvol    |          |
         HC—CMeH—CO
```

is probably the pseudo-form of

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           HC — CPr = CH
Carvacrol   |         |
           HC — CMe = C(OH)
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(Goldschmidt, *B.* 20, 490). According to Gladstone (*C. J.* 49, 621) the presence of two pairs of doubly-linked atoms of carbon in the molecule of carvol is indicated by its molecular refraction.

CARVOXIM $C_{10}H_{14}{:}N(OH)$. *Nitroso-hesperidene or nitroso-carvene.* [71°]. Large colourless transparent plates. Sol. acids and alkalis.

Formation.—1. By the action of hydroxylamine upon carvol.—2. By passing nitrosyl chloride into a methyl-alcoholic solution of carvene, and heating to its melting-point the crystalline hydrochloride $C_{10}H_{16}ONCl$ which precipitates.

Reactions.—1. By heating with dilute H_2SO_4 carvol is regenerated.—2. By passing HCl gas into its methyl-alcoholic solution the oxim of carvol chloro-hydride (*v. supra*) is formed.

Hydrochloride B'HCl; white crystalline solid; decomposed by water; formed by passing HCl into the ethereal solution.

Methyl ether $C_{10}H_{14}{:}N(OMe)$: colourless fluid.

Benzoyl derivative $C_{10}H_{14}{:}N(OBz)$: [95°], white glistening needles, v. sol. alcohol and benzene (Goldschmidt a. Zürrer, *B.* 17, 1577; 18, 1729).

Iso-carvoxim $C_{10}H_{14}(NOH)$. [143°], possibly $CPr\begin{cases}CH.C(NOH)\\CH_2\text{———}CH\end{cases}CMe$. Obtained, together with a small quantity of carvoxim, by the action of excess of hydroxylamine on a solution of carvol chlorohydride or bromo-hydride in alcohol (Goldschmidt a. Kisser, *B.* 20, 2071). Needles, sl. sol. alcohol; sol. acids and alkalis. Unlike carvoxim, it does not combine with HCl or HBr. Dilute H_2SO_4 forms carvacrol and a compound $C_{10}H_{15}NO$ [94°].

Benzoyl derivative $C_{10}H_{14}(NOBz)$: [112°]; scales, v. sol. alcohol.

CARVYLAMINE $C_{10}H_{15}.NH_2$. Formed by reduction of carvoxim $C_{10}H_{14}.NOH$ in alcoholic solution, by sodium-amalgam and acetic acid. Colourless liquid, of strongly aromatic basic odour. Readily absorbs CO_2 from the air.—B'HCl: [c. 180°], slender silky needles (from alcohol).

Benzoyl derivative $C_{10}H_{15}.NHBz$: [169°]; white needles (Goldschmidt a. Kisser, *B.* 20, 486).

CARYOPHYLLIN $C_{40}H_{64}O_4$ (?) A substance that may be extracted by alcohol from cloves, the dried flower-buds of *Caryophyllus aromaticus* (Mylius, *B. J.* 22, 452; Muspratt, *Ph.* 10, 343). Silky needles in stellate groups; sublimes at about 285°. Sl. sol. cold alcohol, sol. boiling alkalis. PCl_5 forms $C_{40}H_{63}O_3Cl$ and $C_{40}H_{63}O_3Cl_3$.

Acetyl derivative [184°]. Monoclinic crystals (Hjelt, *B.* 13, 800).

Caryophyllic acid $C_{40}H_{64}O_{12}$. From caryophyllin and fuming HNO_3 (Mylius, *B.* 6, 1053). Amorphous; sl. sol. water, v. sol. alcohol, ether, and HOAc. May be crystallised from fuming HNO_3.

Salts. $-Na_4A''''$. $-Ag_4A''''$. $-Ba_2A''''$ $1\frac{1}{2}$aq.

CASCARILLIN $C_{12}H_{18}O_4$. [205°]. S. ·127 at 100°; S. (alcohol) 3·33 at 8°. Extracted from cascarilla bark (from *Croton Eleutheria* and *Cascarilla*) by boiling water (Mylius, *B.* 6, 1051; *cf.* Tuson, *C. J.* 17, 195; Duval, *J. Ph.* [3] 8, 91). Minute prisms (from alcohol); tastes bitter. Not affected by boiling dilute HCl. Cascarilla bark also contains a volatile oil (173°-180°).

CASEÏN *v.* PROTEÏDS.

CASEOSE *v.* PROTEÏDS.

CASSONIC ACID $C_6H_8O_7$. Formed, together with saccharic and oxalic acids, in the oxidation of cane sugar by HNO_3 (Siewert, *Institut.* 21, 78). Also from glyconic acid and HNO_3 (Hönig, *J.* 1879, 667). Syrup. Reduces ammoniacal $AgNO_3$ to a mirror.—BaA″xaq.

CASTORIN. Castoreum is a hard black substance (soft when fresh) found in a pair of small sacs situated in the genital organs of the beaver (*Castor fiber* and *americanus*). An alcoholic extract deposits first fat, and then castorin. Castoreum also contains a volatile pungent oil,

cholesterin, a resin, proteïds, $CaCO_3$, and inorganic salts (Valenciennes, *J.* 1861, 803).

CASTOR OIL. A fatty oil obtained by pressure from the seeds of *Ricinus communis*. It solidifies at about −18°, has S.G. about ·969 at 12°, and is dextro-rotatory, [α] = 12° (Popp, *Ar. Ph.* [2] 145, 233). Castor oil consists chiefly of glycerides of stearic and ricinoleïc acids. It is completely dissolved by 5 vols. of 90 p.c. alcohol (Hager, *C. C.* 1876, 389). Dry distillation gives acroleïn, œnanthol (heptoic aldehyde) and an acid $(C_{11}H_{20}O_2)_x$ (Bussy a. Lecanu, *J. Ph.* 13, 57; Stanek, *J. pr.* 63, 138; Leeds, *B.* 16, 290; Krafft a. Brunner, *B.* 17, 2985). HNO_3 oxidises it to heptoic, oxalic, azelaïc, suberic, and (β)-pimelic acids (Arppe, *A.* 120, 288). The products obtained by saponifying castor-oil and distilling the resulting alkaline ricinoleate alone or with NaOH are methyl hexyl ketone, *sec*-octyl alcohol, and sebacic acid (Neison, *C. J.* 27, 507, 837). Conc. H_2SO_4 converts castor oil into ricinyl-sulphuric acid $C_{18}H_{33}O_2OSO_3H$, which by the addition of water breaks up into ricinoleïc acid and H_2SO_4. From the fatty acids derived from the Turkey-red oil prepared from castor oil, crystals of a di-oxy-stearic acid separate after some time (Benedikt a. Ulzer, *M.* 8, 217).

CATALPIC ACID $C_{14}H_{14}O_6$. [206°]. Extracted by ether from decoctions of the siliquaceous capsule of the *Bignonia Catalpa*. It may be isomeric with hydrocardenic acid (Sardo, *G.* 14, 134). Large white crystals, v. sl. sol. water, sol. alcohol and ether. – $BaC_{14}H_{12}O_6$ 6aq: white glistening laminæ.—Ag_2A'': a white pp.

CATALYSIS *v.* CHEMICAL CHANGE.

CATECHINS $C_{19}H_{18}O_8$ 3aq (Hlasiwetz; Cross a. Bevan, *C. J.* 41, 92); $C_{18}H_{18}O_8$ (Etti, *M.* 2, 547); $C_{21}H_{20}O_9$ (Liebermann a. Tauchert, *B.* 13, 694); $C_{40}H_{38}O_{16}$ and $C_{42}H_{38}O_{16}$ (Gautier, *C. R.* 85, 668). This name has been given to various compounds contained in catechu or Terra japonica which is extracted by boiling water from the fruits or twigs of a variety of plants: Bombay catechu from the fruit of *Areca Catechu*, Bengal catechu from twigs and unripe pods of *Acacia* (or *Mimosa*) *Catechu*, Gambir catechu from *Nauclea* (*Uncaria*) *Gambir*, and Nubian catechu from some *Acacia*. Catechu is used in dyeing.

Catechin $C_{21}H_{18}O_8$ (Gautier, *C. R.* 85, 752); $C_{19}H_{18}O_8$ 3aq (C. a. B.); $C_{21}H_{20}O_9$ 5aq (L. a. T.). [217°]. S. (alcohol) 20 at 15°; S. (ether) ·8 at 15° (Wackenroder, *A.* 37, 311). Obtained from Bombay catechu by washing with water and crystallising from acetic ether (L. a. T.; Löwe, *Fr.* 13, 113; Zwenger, *A.* 37, 320; Neubauer, *A.* 96, 337; Kraut a. Van Delden, *A.* 128, 285; Hlasiwetz a. Malin, *A.* 134, 118; Etti, *A.* 186, 337; Schützenberger, *Bl.* [2] 4, 5; Sace, *C. R.* 53, 1102).

Properties.—Small needles (from water). V. sl. sol. cold water, v. sol. hot water and acetic ether. The aqueous solution is coloured green by Fe_2Cl_6. The solution in KOHAq absorbs oxygen, turning brown. Lead acetate gives in aqueous solution a pp. of $(C_{21}H_{20}O_9)_2 3PbO$ (?) Catechin solutions are ppd. by albumen, but not by gelatin.

Reactions.—1. Boiling dilute H_2SO_4 forms catechuretin.—2. With HCl and $KClO_3$ it gives $C_{20}H_{10}Cl_4O_{12}$? (Cross a. Bevan, *C. J.* 41, 92) which is turned crimson by Na_2SO_3. Catechutannic acid does the same.—3. Br gives bromo-catechuretin $C_{21}H_8Br_7O_7$?, a red insoluble powder. 4. Water and PI_3 give $C_{21}H_{20}O_8$, an elastic insoluble mass.—5. HOAc and BaO_2 give $C_{21}H_{20}O_{10}$ a colourless powder which melts below 100° (Schützenberger a. Rack, *Bl.* 4, 8).—6. Aqueous $K_2Cr_2O_7$ forms $C_{21}H_{14}O_{10}$, a brown insoluble powder.—7. *Potash-fusion* gives phloroglucin and protocatechuic acid (Hlasiwetz, *A.* 134, 118).—8. *Dry distillation* gives pyrocatechin.—9. Boiling dilute H_2SO_4 forms insoluble $C_{21}H_{16}O_7$ (Neubauer, *A.* 96, 356), or $C_{38}H_{30}O_{12}$ (Etti).—10. Boiling dilute KOH forms $C_{21}H_{18}O_8$(?) a brown powder, sol. alcohol and alkalis.—11. HI gives iodoform and other products (G.).

Di-acetyl derivative $C_{21}H_{18}O_7(OAc)_2$: [131°]; needles or prisms. Soluble in ordinary solvents except water and ligroïn (L. a. T.).

Di-benzoyl derivative $C_{21}H_{18}O_7(OBz)_2$. Flocculent brown substance (S. a. R.).

Diacetyl-dichloro-catechin $C_{21}H_{16}Cl_2(OAc)_2O_7$: [169°]; needles. Sol. alcohol, sl. sol. ether.

Diacetyl-bromo-catechin $C_{21}H_{17}Br(OAc)_2O_7$; [120°]. White needles. Sol. alcohol, sl. sol. ether.

Catechuretin $C_{42}H_{30}O_{13}$ 6aq(?) or $C_{38}H_{28}O_{12}$. Formed by passing HCl into a boiling alcoholic solution of catechin (Kraut a. Delden, *A.* 128, 291). Formed also by heating catechin with conc. HCl at 170°. Dark reddish-brown insoluble powder. Not changed at 190°.

Di-benzoyl derivative $C_{21}H_{14}Bz_2O_7$(?) Formed, together with di-benzoyl-catechin by heating catechin with BzCl at 190°. Brown mass.

Catechin $C_{40}H_{38}O_{16}$ 2aq. [205°]. S. 9·9 at 50°. Occurs according to Gautier (*C. R.* 86, 668) in Gambir-catechu together with the two following catechins; they are extracted by alcohol and crystallised after evaporation with exclusion of air. Monoclinic prisms.

Catechin $C_{42}H_{38}O_{16}$ aq. [177°]. Minute needles (*v. supra*).

Catechin $C_{40}H_{38}O_{16}$ aq. [163°]. S. 5·3 at 50°. Minute needles (*v. supra*).

Catechin $C_{18}H_{18}O_8$ aq. According to Etti (*M.* 2, 547) this is the formula of the catechin in Gambir and Pegu catechins. At 100° it becomes $C_{18}H_{16}O_8$, at 160° catechutannic acid $C_{36}H_{34}O_{15}$ and at 180° $C_{36}H_{32}O_{14}$. The latter is also got by heating catechin for some time with dilute H_2SO_4.

Reactions. -1. *Diazobenzene chloride* gives $(C_6H_5N_2)_2C_{18}H_{16}O_8$, a red crystalline pp. sol. alcohol and ether; it dyes wool golden-brown.—2. Dilute H_2SO_4 (1:8) at 140° gives phloroglucin and pyrocatechin.

Catechin $C_{42}H_{41}O_{16}$. [165°]. In mahogany (*Acajou*) (Gautier, *Bl.* [2] 30, 568). Latour a. Cazeneuve (*Bl.* [2] 24, 119) give this catechin the formula $C_{20}H_{20}O_9$.

Catechin $C_{42}H_{36}O_{16}$. [140°]. In brown catechu (G.).

CATECHOL *v.* PYROCATECHIN.

CATECHUIC ACID *v.* CATECHIN and PROTOCATECHUIC ACID.

CATECHUTANNIC ACID $C_{21}H_{18}O_8$(?) or $C_{38}H_{34}O_{15}$(?) Extracted by water from catechu.

Formed also by heating catechin alone at 130°, with water at 110°, or by boiling it with alkalis, lime, or $Pb(OH)_2$ (Etti, *A.* 186, 332; Löwe, *J. pr.* 105, 32, 75; *Z.* [2] 5, 538; *Fr.* 12, 285). Dark reddish-brown powder. V. sol. acetic ether, v. e. sol. alcohol, insol. ether; m. sol. water. It oxidises in the air. It gives a greyish-green pp. with Fe_2Cl_6. It does not pp. tartar-emetic. Its aqueous solution is pd. by gelatin, albumen, and by dilute H_2SO_4. At 162° it changes to $C_{42}H_{34}O_{17}$(?) which resembles catechutannic acid in all respects $-(C_{21}H_{18}O_8)_2 3PbO$.

CATHARTIC ACID. The active principle in senna leaves. It is a glucoside. It contains only C, H, and O. Its Ba and Pb salts are amorphous (Kubly, *Bl.* [2] 7, 356; Stockman, *Ph.* [3] 15, 749; *cf.* Lassaigne a. Feneuille, *A. Ch.* [2] 16, 18; Bourgoin, *C. R.* 73, 1449).

CAULOSTERIN *v.* CHOLESTERIN.

CEDAR OIL. Obtained by distilling with water the wood of *Juniperus virginiana.* Contains cedrene and cedar-camphor. According to Bertagnini (*C. R.* 35, 800) it contains a compound which combines with $NaHSO_3$.

Cedar-camphor $C_{15}H_{26}O$. [74°]. (282°). V.D. 8·4 (calc. 7·7). Crystalline mass smelling like cedar-wood. V. sl. sol. water, v. sol. alcohol. Distillation with P_2O_5 splits it up into water and cedrene (Walter, *A. Ch.* [3] 1, 498).

CEDRENE $C_{15}H_{24}$. (237°). S.V. 7·6. S.G. $\frac{15}{}$ ·984. Obtained as above (Walter, *l.c.*).

Cedrene. *From oil of sage* (English). $C_{15}H_{24}$. (260°). S.G. $\frac{15}{}$ ·915. Yellow or green oil. Inactive. Resinified by H_2SO_4 (4:1) even at 0°. Gaseous HCl turns an ethereal solution purple. The refractive index seems to indicate four C:C groups (M. M. P. Muir, *C. J.* 37, 686).

The name Cedrene has been used as a generic name for the hydrocarbons $C_{15}H_{24}$ which occur in the oils of cedar, cloves, patchouli, cubebs, calamus, cascarilla, rosewood, &c. (*v.* TERPENES). Cedrenes closely resemble the terpenes in their optical properties, which point to the existence of $1\frac{1}{2}$ pairs of doubly linked carbon atoms (Gladstone, *C. J.* 49, 617).

CEDRIRET *v.* CŒRULIGNON.

CELLULOSE. $_n\{C_6H_{10}O_5\}$. S.G. 1·25-1·45.

Occurrence.—Cellulose is the basal substance of the skeleton of plants, and indeed may be said to constitute the framework of the vegetable world. The problem of its origin is as much physiological as chemical. It does not appear to be formed as the immediate product of the synthetical action of the cell upon carbonic anhydride and water, but mediately from starch, sugar, and other carbohydrates, through the intervention of the cell protoplasm. The mechanism of this transformation, as well as the inverse conversion of cellulose into the simpler carbohydrates, has not been elucidated, but is assumed on physiological grounds to be of the simplest character. There is nothing in this assumption which contravenes the evidence afforded by the chemical relationships of the carbohydrate group, which are likewise simple.

Adapting itself to the infinite variety of structure and function presented by plant tissues, cellulose occurs in multitudinous forms: and in any given structure is subject to differentiation, modification, or variation of elaboration within very wide limits. The scope of this article, however, precludes such a treatment of the subject as would deal with lesser variations, and we shall therefore confine our attention to those celluloses which constitute the fully elaborated plant fibres. Plant tissues seldom if ever consist of pure cellulose but contain besides other products of growth, either mechanically bound up with the tissue, and therefore frequently removable by mechanical means and by the action of simple solvents, or *chemically* united to the cellulose; combinations of this latter kind constitute the *compound celluloses*, and are only resolved by a *chemical* process.

Preparation.—The isolation of pure cellulose depends upon its relative insusceptibility of chemical change. The general method of preparation from raw fibrous materials consists in exposing the moist fibre or tissue to the action of chlorine gas or bromine-water in the cold and subsequently boiling in a dilute alkaline solution; repeating this treatment until the alkaline solution no longer dissolves anything from the tissue or fibre. The cellulose is then washed with a dilute acid, water, alcohol, and ether, and dried.

Properties.—Obtained in this way, or by the ordinary process of bleaching from cotton or linen (flax), or in the form of Swedish filter paper, the typical cellulose is a white substance more or less transparent,[1] retaining the microscopic features of the raw fibre.

The elementary composition is expressed by the percentage numbers (F. Schulze):

C	44·0	44·2
H	6·4	6·3
O	49·6	49·5

or by the corresponding empirical formula $C_6H_{10}O_5$. These numbers represent the composition of the dry and ash-free cellulose. Nearly all celluloses contain a certain proportion, however small, of *mineral constituents*[2] and the union of these with the organic portion of the fibre or tissue is of such a nature that the ash left on ignition preserves the form of the original. It is only in the growing point of certain young shoots that the cellulose tissue is sometimes found free from mineral constituents (Hofmeister). The proportion of *hygroscopic moisture*, which is an essential constituent of cellulose under ordinary atmospheric conditions, varies from 7 to 9 p.c.; the mean variation due to variations in the hygrometric state of the air is about 1 p.c.

Cellulose is insoluble in all simple solvents; it is dissolved by certain reagents but only by virtue of a preceding constitutional modification. The most remarkable solvent of cellulose is *cuprammonia* (Schweitzer's reagent) in which it dissolves without essential modification, being recovered by precipitation in a form which is chemically identical with the original (Erdmann, *J. pr.* 76, 385), though differing in being amor-

[1] Cellulose in its earlier stage of elaboration has no action upon light, but with age it acquires the property of double refraction. This action is independent of the state of aggregation of the cellulose and is therefore an essential property of the substance itself (Sachs, *Exp. Phys. d. Pflanzen*, p. 398).

[2] The inorganic constituents of bleached cotton amount to 0·1-0·2 p.c. of its weight. In the manufacture of the so-called Swedish paper, the proportion is reduced by special treatment of the cellulose with acids.

phous. This reagent has been employed in a variety of forms, a fact which explains the discrepancies in the statements as to the solubilities of the various celluloses in cuprammonia. The following methods of applying the reagent are to be recommended.

The substance to be operated upon is intimately mixed with copper turnings in a tube which is narrowed below and provided with a stopcock. Strong ammonia is poured upon the contents of the tube and after standing for some minutes is drawn off and returned to the tube; the operation is several times repeated until the solution of the substance is effected.

Perhaps the most convenient solution, though not so effective in all cases as the former, is that prepared by dissolving ppd. cupric hydrate in ammonia. In preparing the reagent in this way it is important that the hydrate should be thoroughly washed, preferably out of contact with the air, before dissolving in the strong aqueous ammonia. Cotton is rapidly dissolved by this solution. The soluble compound formed is represented by Mulder as $(C_6H_{10}O_5)_2Cu(NH_4)_2O$. It has been doubted whether this compound exists actually dissolved in the viscous solution; an investigation of the osmotic properties of the liquid, however, shows it to be a true solution (Cramer). From an extended investigation of the optical properties of the solution Béchamp concludes that the solution of the cellulose is not simple but is accompanied by progressive molecular transformations, the optical activity (dextrorotatory) of the products increasing to a maximum corresponding to a condition of equilibrium ultimately attained (*C. R.* 100, 117, 279, 368).

The soluble bases (NaOH, KOH) added to the solution give blue gelatinous pps. having the composition $(C_6H_{10}O_5)_2CuM''O$. Digested with finely divided lead oxide the solution yields the compound $C_6H_{10}O_5.PbO$. Cellulose is reppd., as a gelatinous hydrate, on the addition of acids, as well as of many neutral bodies such as alcohol, suga , and common salt, or even on largely diluting with water and allowing to stand. The pp. dried *in vacuo* is obtained as a transparent mass resembling gum-arabic. On digesting the ammonia-cupric solution upon metallic zinc, this metal pps. the copper, replacing it in the solution and producing the corresponding ammonia-zincic solution of cellulose, which is colourless. The property of cellulose of being dissolved by cuprammonia receives an important technical application. A sheet of paper left for a short time in contact with the cuprammonia, so that the constituent fibres are superficially attacked, and then passed between rollers and dried, becomes impervious to water and its cohesion is not affected at the boiling heat. Two sheets thus treated adhere firmly together, and with a sufficient number, artificial boards are produced. A variety of materials are now produced in this way, on the manufacturing scale, useful for roofing and other purposes (C. R. A. Wright, *Journ. Soc. Chem. Ind.* 1884, p. 121).

Reactions.—Cellulose has already been spoken of as a comparatively inert substance, and its characteristic reactions are consequently few. One of these is available for its identification and is chiefly used in the microscopical examinations of tissues: this is its reaction with iodine. The reaction, although similar to that of starch, differs in requiring for its determination the presence of an auxiliary (dehydrating) reagent such as sulphuric or phosphoric acid or zinc chloride. The most effective solution is prepared in the following way: zinc is dissolved to saturation in hydrochloric acid and the solution evaporated to the sp. gr. 2·0; to 90 pts. of this solution are added 6 pts. potassium iodide dissolved in 10 pts. water and in this solution iodine is dissolved to saturation. By this reagent cellulose is coloured instantly a deep blue or violet.

COMPOUNDS OF CELLULOSE.—Cellulose is generally inactive towards compounds contained in dilute aqueous solution; hence its extensive employment in the filtration of solids from solutions. Nevertheless it exhibits a tendency to incipient combination even with acids and alkalis (Mills, *C. J.* 43, 153); with metallic salts it forms compounds of sufficient stability to cause their removal from solution, but the combination is of an indefinite and unstable order (Erdmann, *J. pr.* 76, 385). (*Cf.* Gladstone, *J. pr.* 56, 217; Müller, *Fr.* 1, 84; O'Shea, *C. J. Proc.* 1, 206.) Certain carbon compounds, such as the organic astringents, and many of the colouring matters natural and artificial, unite with cellulose to form compounds of various orders of stability; of these we would more particularly instance amongst others many of the derivatives of diphenyl which possess a specific power of direct combination with cellulose. Although such combinations are of great technical importance, being the foundation of the arts of dyeing and printing they are not sufficiently systematised to deserve more than this passing notice. On the other hand some of the substitution-compounds of cellulose with acid radicles are both definite and stable.

Acetyl-cellulose.—The tri-substituted compound $C_6H_7(C_2H_3O)_3O_5$ is formed by heating cellulose with 6–8 times its weight of acetic anhydride at 180°, and separates as a white flocculent pp. on diluting the syrupy product. Tri-acetyl-cellulose is insoluble in alcohol and in ether, and is soluble in glacial acetic acid. It is saponified by boiling with alkaline solutions, the cellulose being regenerated. No derivative containing more than three acetyl groups has been obtained; but a mixture of the mono- and di-acetyl cellulose is formed by treating cellulose with only twice its weight of acetic anhydride, the formation of these bodies being unattended by their solution.

Cellulose nitrates. (*Pyroxylin—Nitrocellulose.*)—Whenever cellulose in any form is brought into contact with strong nitric acid at a low temperature, a nitro-product or nitrate is formed. The extent of the nitration depends upon the concentration of the acid, upon the duration of its contact with the cellulose, and on the state of the physical division of the cellulose itself. The first investigation of these substances dates from 1838, when Pelouze showed the identity of several of these products obtained from paper, linen &c. and starch. Knop and also Kamarsch and Heeren found that a mixture of sulphuric and nitric acids also formed nitrate of cellulose; and still later (1847) Millon and Gaudin employed a mixture of sulphuric

acid and nitrate of potash and soda, which they found to have the same effect. Although gun-cottons or pyroxylines are generally spoken of as nitro-celluloses, they are more correctly described as cellulose nitrates, since they have not been found to yield amido-bodies on reduction with nascent hydrogen. The following are the general properties of these compounds (Eder): (1) When warmed with alkaline solutions, nitric acid is removed in varying quantities, dependent upon the strength of the solution employed. (2) Treatment with cold concentrated sulphuric acid expels almost the whole of the nitric acid. (3) On boiling with ferrous sulphate and hydrochloric acid, the nitrogen is expelled as nitric oxide; this reaction is used as a method of nitrogen estimation in these bodies. (4) Potassium sulphydrate, ferrous acetate, and many other substances, reconvert the nitrates into cellulose.

Several well-characterised nitrates have been obtained, but it is a matter of difficulty to prepare any one in a state of purity and without admixture of a higher or lower nitrated body. The following have been described under a nomenclature having reference to a C_{12} formula:

Hexa-nitrate.—$C_{12}H_{14}(NO_3)_6O_4$ (gun-cotton). Prepared by treating cotton with a mixture of HNO_3 (S.G. 1·5) 3 parts, and H_2SO_4 (S.G. 1·84) 1 part, for 24 hours, at a temperature not exceeding 10°; 100 parts of cellulose yield about 175 of the compound (calc. 183). Insoluble in alcohol, ether, or mixtures of both, and glacial acetic acid; with acetone it forms a jelly and is slowly dissolved. It is the most explosive of the series igniting at 160°–170°. Mixtures of sulphuric acid and nitre do not give this nitrate (Eder). Ordinary gun-cotton may contain as much as 12 p.c. of nitrates soluble in ether-alcohol; the hexa-nitrate seems to be the only one quite insoluble in this menstruum.

Penta-nitrate.—$C_{12}H_{15}(NO_3)_5O_5$. This composition has been very commonly ascribed to gun-cotton. It is impossible to prepare it in a state of purity by the direct action of the acid on cellulose. It is prepared by dissolving the hexa-nitrate in nitric acid at 80°–90°, cooling to 0°, and adding concentrated sulphuric acid, by which the penta-nitrate is precipitated; after mixing with a large volume of water and washing the precipitate with water and alcohol, it is dissolved in ether-alcohol and finally re-precipitated by water. This nitrate is slightly soluble in acetic acid, nearly insoluble in alcohol containing only a small proportion of ether. Strong potash solution converts it into the di-nitrate.

Tetra- and tri-nitrates (collodion pyroxyline) are generally formed together when cellulose is treated with a more dilute acid at a higher temperature and for a shorter time than in the case of the hexa-nitrate, *e.g.* 4 vols. HNO_3 (1·38), 5 vols. H_2SO_4 (1·84) at 65°–70° for 5 10 minutes. They are freely and equally soluble in ether-alcohol, acetic ether, and mixtures of acetic acid and wood spirit, or alcohol, and are therefore inseparable. They are insoluble in pure alcohol, ether, or acetic acid. On treatment with concentrated nitric and sulphuric acids they are converted into the higher nitrates. Potash and ammonia convert them into the dinitrate.

Di-nitrate $C_{12}H_{18}(NO_3)_2O_8$ is formed as already indicated, and also by the action of hot dilute nitric acid on cellulose. Freely soluble in ether-alcohol, acetic ether, acetic acid, wood spirit, acetone, and absolute alcohol. The further action of alkalis on the dinitrate results in a complete resolution of the molecule.

The cellulose nitrates have generally much stronger absorption-affinities for colouring matters than the celluloses. They are much less susceptible of attack by acid oxidants than cellulose itself, and are therefore used in the filtration of solutions containing *e.g.* chromic acid, permanganates, and, of course, nitric acid of any degree of concentration. Nitric acid of S.G. 1·42 has a remarkable toughening action upon filter paper: the modification is effected by simple immersion, and the paper so treated is increased in strength tenfold, undergoing at the same time a contraction amounting, in circles, to about $\frac{1}{10}$ diameter. The cellulose so treated contains no nitrogen (Francis, *C. J.* 47, 183).

Cellulose and sulphuric acid.—Cellulose is disintegrated and dissolved by the concentrated acid to a colourless solution. The products are sulphates of a series of compounds of which the celluloses and the dextrins may be regarded as the extreme terms. They are easily isolated in the form of Ba salts. The composition of the sulphates may be expressed by the general formula $C_{6n}H_{10n}O_{5n-x}(SO_4)_x$. The variations in composition and in physical properties are functions of the temperature (5°–35°) and duration of the action. The limits of specific rotation of these sulphates are $[\alpha]_j = -3·65$ and $+72·99$. These ethereal salts are entirely decomposed by boiling with alcohol: the resulting carbohydrates may be regarded as the corresponding alcohols. In composition and properties (*e.g.* their reactions with iodine) they constitute an extended series, beginning with soluble celluloses and terminating in achrodextrin (Hönig a. Schubert, *M.* 7, 455). While it is impossible to determine the mechanism of these successive resolutions of the cellulose molecule with the precision attainable where such changes may be reversed, and therefore completely studied, they certainly establish the typical connection of the celluloses with the simpler carbohydrates, and in a much more complete way than the coincidence of empirical formulæ.

Prior to the researches above detailed the initial terms of the transition series had been similarly obtained and described under the term *Amyloid*, a term selected to indicate their resemblance to starch.

A practical application of the reaction of cellulose with sulphuric acid is found in the manufacture of *parchment paper*. The process consists in the rapid passage of the paper through the strong acid (S.G. 1·5–1·6) followed by copious washing. The result may be described as a superficial conversion of the cellulose into amyloid, whereby it acquires the properties which have obtained for it the designation in question (*cf.* Hofmann, *A.* 112, 243).

Cellulose and chlorine.—Dry chlorine has no action upon cellulose; the presence of water determines an indirect oxidising action, but there is no direct combination of cellulose with

chlorine. By heating cellulose nitrates with phosphoric pentachloride and oxychloride at 200° and evaporating the excess of the reagents at 170°, a viscous liquid is left, miscible with alcohol and ether, which appears to be composed of, or to contain, a chloride of cellulose or a cellulose derivative (Baeyer, *B.* 2, 54). *Bromine* is without action upon cellulose: specimens left for several months in contact with strong bromine-water were not sensibly attacked (H. Müller, *Pflanzenfaser*, p. 27; *cf.* Franchimont, *R. T. C.* 2, 91).

Cellulose and Oxygen. *Oxycelluloses.*—Two of these compounds or series of compounds have been described.

(α)-*Oxycellulose* (Witz, *Bull. Rouen*, 10, 416; 11, 189) is formed by the action of solutions of the hypochlorites upon cellulose. Exposed to the action of a solution of bleaching powder (5 p.c.) for 24 hours, the fibre is converted into a friable modification having the composition C 43·0, H 6·2, O 50·8. Other oxidising agents produce similar results; even by exposure to air and light cellulose is slowly converted into these oxidised derivatives. Their formation is accompanied by molecular resolution, as is shown by their reducing action upon alkaline copper solutions: the product giving this reaction is dissolved by alkalis to a yellow solution. These oxycelluloses have a strong attraction for basic colouring matters: also for vanadium compounds, attracting these from a solution containing so minute a quantity as 1 pt. in 1,000,000,000. Upon this property a method has been founded for the quantitative estimation of minute traces of vanadium in aqueous solution (Witz a. Osmond, *Bull. Rouen*, 14, 30). The study of these oxycelluloses is of great importance to the manufacturer of textile materials.

(β)-*Oxycellulose* $C_{18}H_{26}O_{16}$ (Cross a. Bevan, *C. J.* 43, 22) is the residual product (insoluble) of the prolonged digestion of cellulose with nitric acid (20-30 p.c.) at 90° C. On washing with water to remove the acid the substance gelatinises. It dries to a horny colourless mass. It is characterised by its reaction with sulphuric acid: on gently warming it dissolves with development of a bright pink colour, the reaction resembling that of mucic acid, to which, on other grounds, it is probably related. A fresh preparation, treated with a mixture of nitric and sulphuric acids, dissolves, and on pouring into water the nitrate $C_{18}H_{23}(NO_3)_3O_{13}$ separates as a white flocculent pp.

Chromic acid.—Cellulose treated with potassium dichromate in presence of acetic acid is converted into glucose, dextrin, and formic acid. Permanganates under the same condition effect a similar decomposition.

Chromic anhydride in presence of sulphuric acid decomposes cellulose rapidly and completely, the carbon being entirely converted into the gaseous compounds CO and CO_2. It has been proposed to apply this to the quantitative estimation of carbon in celluloses and cellulosic mixtures (Cross a. Bevan, *C. N.* 52, 207).

Alkaline oxidations.—The permanganates and hypochlorites in presence of alkalis oxidise cellulose to a syrupy mixture of acids of the pectic series (H. Müller, *Pflanzenfaser*, *v.* also *S. C. I.* 8, 206, 291). Fused with potassium hydrate the cellulose is oxidised to oxalic acid, malic acid being obtained as an intermediate product.

Electrolytic oxidants.—The nascent oxygen and other electronegative ions liberated in the electrolysis of various saline solutions have a very powerful action upon cellulose. These actions have been made the subject of interesting researches by F. Goppelsroeder (*D. P. J.* 254, 42).

Cellulose and Hydrolytic Agents.

(1) *Dilute acids.* A large number of acids, organic as well as mineral, attack cellulose, producing hydration changes, attended by disintegration of the fibre. The action is gradual at ordinary temperatures, and is of course accelerated by applying heat. The study of these actions is of the first importance to the cellulose technologist (Girard, *C. R.* 81, 1105; Cross a. Bevan, *S. C. I.* 1885; Crookes, *Handbook of Dyeing and Calico-printing*, p. 19).

It is worthy of note here that the cellulose isolated from grass and hay, and many others less highly elaborated than the celluloses which we are at present considering (cotton and linen), are decomposed on boiling with dilute mineral acids with formation of furfural.

(2) *Alkalis.*—Dilute solutions of the alkalis are without sensible action upon cellulose, even at temperatures considerably above the boiling point: when, however, oxidising conditions are superadded, molecular resolution sets in. The joint action of calcium hydrate and air at the boiling temperature is especially powerful, oxycellulose being produced (Witz, *loc. cit.*). Concentrated solutions of the alkalis (NaOH, KOH) at ordinary temperatures act in a very remarkable way upon cellulose. There appears to be a 'molecular' combination of the reagents in the proportion $C_{12}H_{20}O_{10}{:}Na_2O$ (Mercer) which however is easily resolved by washing with water. But the characteristics of the fibre and the fibre substance are found to have undergone a permanent modification. There is a considerable shrinkage in linear dimensions: in cotton fabrics treated with caustic soda solution of S.G. 1·225 this amounts to 25 p.c. The corresponding modifications in microscopic features have been investigated by Crum (*C. J.* 1863), the changes being found similar to those which take place in the ripening of the fibre in the plant, viz. from a flattened tube with large central cavity, to a thick-walled cylinder with small lumen. The chemical change produced is, so far as has been ascertained, entirely one of hydration, and it is remarkable that the only evidence of the change is the increased capacity for hygroscopic moisture. This amounts to 5 p.c. of the weight of the cotton, the proportion calculated for the formula $C_{12}H_{20}O_{10}.H_2O$ being 5·5 p.c. From this fact we may also infer that the normal attraction of cellulose for atmospheric moisture is a residual manifestation of the molecular combinations which are seen in the multitudinous hydrates of cellulose found in, or constituting, growing tissues. Mercer, who appears to have first investigated these phenomena, further found that the addition of hydrated oxide of zinc very much increased the action of the caustic solution: thus a solution of sodium hydrate of S.G. 1·100, which is without marked action, is rendered very active by

the addition of the oxide in the proportion $ZnO:2Na_2O$. He also found that the actions were favoured by low temperatures (*v. Life of John Mercer* by E. A. Parnell, London, 1886).

By these characteristics the hydration phenomena in question are seen to be closely related to those attending the action of the Schweitzer reagent (*supra*). The more powerful action of the latter we must refer either to the specific action of the ammonia upon the condensed aldehydic molecules of which cellulose appears to be constituted, or to the particular relationship of the molecular weight of the cuprammonia in solution to that of the cellulose or cellulose hydrate which it forms.

The action of concentrated solutions of zinc chloride is similar to that of the alkaline hydrates above hydrates. It is remarkable on the other hand that a saturated solution of zinc nitrate is without action (Mercer).

(3) *Water.*—Heated in contact with water, cellulose is attacked at 160°, but not below 150° (Scheurer a. Grosseteste, *Bull. Mulhouse*, 1883, 62-85). Heated at 200° in contact with water in sealed glass tubes it is fundamentally resolved, being converted into highly-coloured products, insoluble for the most part, with a small proportion of soluble derivatives amongst which are furfural and pyrocatechol (Hoppe-Seyler, *B.* 4, 15).

(4) *Ferments.*—There are, it can scarcely be doubted, endless transformations of cellulose determined by the so-called soluble ferments, though but few have been investigated. The soluble ferment of the foxglove is stated to convert cellulose into glucose and dextrin (Kosmann, *Bl.* [2] 27, 246). The fluid from the vermiform appendix of the rabbit has also been found to digest cellulose with liberation of marsh gas and formation of a soluble compound which reduces cupric oxide in alkaline solution.

Proximate Syntheses of Cellulose.—Transformations of the soluble carbohydrates into cellulose, which we may regard as a proximate synthesis of this body, are, as already stated, an important feature in the life of plants. The mechanism of these changes has been thus far but slightly studied, and they are of a kind to elude chemical investigation. Of those which have been studied we may notice (a) There is a change set up 'spontaneously' in beet juice which results in the formation of a hard white substance, having the properties of cellulose. On transferring these lumps to a solution of pure cane sugar, a further transformation of the saccharose into the same substance is brought about. At the same time there is produced a gummy substance which is ppd. by alcohol as a white caoutchouc-like substance of the same composition as cellulose but swelling up with water and otherwise differing in its physical properties from cellulose. This latter derivative is also formed by the action of diastase upon a solution of saccharose. A similar transformation takes place under the influence of certain fatty seeds, *e.g.* those of rape and colza, and it is probable that the formation of cellulose from saccharose in the plant takes place under the influence of ferments similar to those above described (Durin, *C. R.* 82, 1108).

(b) More recently A. Brown has investigated the formation of cellulose by the 'vinegar-plant,' growing in solutions of the carbohydrates, *e.g.* dextrose in yeast-water. The cells elaborate an extra-cellular film, which acts as a 'cell-collecting medium,' and they possess, therefore, a two sided activity, *i.e.* the property above mentioned, in addition to their strictly fermentative activity. The cellulosic film in question was found to contain 50-60 p.c. pure cellulose. It is noteworthy that in a solution of levulose the growth of the 'plant' is unattended by fermentative action, 33 p.c. of the substance being on the other hand transformed into cellulose (*C. J.* 48, 432).

OTHER FORMS OF CELLULOSE.

We cannot attempt to enumerate the multitudinous varieties of cellulose which the plant world presents. Some of these, when isolated in the pure state, resemble the typical cellulose above described, *e.g.* the cellulose of hemp and rhea. Others, especially such as require a drastic process of resolution, *e.g.* the cellulose isolated from jute and wood by the chlorination method (*infra*), resemble rather the (a)-oxycelluloses. Thus jute cellulose ($3C_6H_{10}O_5.H_2O$) reduces cupric oxide in alkaline solution, and is much more susceptible of degradation by hydrolytic reagents than those of the cotton type. Cellulose from pinewood is similar in composition and properties.

Cellulose from esparto and straw, isolated by treatment of the plant substance with alkaline solutions boiling under pressure—which are amongst the most important of the staple materials of the paper-maker—are distinguished by their reaction with aniline salts, being coloured a deep pink on boiling with solutions of these compounds. Many of the celluloses are decomposed on boiling with dilute acids with formation of furfural and formic acid: hay cellulose yields under certain conditions a volatile crystalline body, which appears to be a furfural derivative, but is still under investigation.

It may be mentioned here that the term cellulose is applied by plant physiologists and agricultural chemists to substances which would not come under the definition, upon which this article is based, of cellulose as the (white) insoluble residue which survives the exhaustive treatment of plant substances alternately with chlorine, bromine, or oxidising agents, and boiling alkaline solutions.

Animal cellulose.—The mantles of the Pyrosomidæ, Salpidæ, and Phallusia mammilaris, freed from chondrigen by boiling in a Papin's digester and further purified by prolonged boiling with potash solution, yields a residual substance which not only has the ultimate composition of cellulose, but has identical properties, *e.g.* dissolves in cuprammonia, is converted by nitric acid into an explosive nitrate soluble in ether (Schäfer, *A.* 160, 312). According to Virchow cellulose is found in degenerated human spleen and in certain parts of the brain (*C. R.* 37, 492, 860).

COMPOUND CELLULOSES.

Plant tissues, always containing a proportion of cellulose more or less large, frequently contain other constituents so intimately united to

the cellulose as to mask its reactions. From the circumstances of their occurrence and formation it is not to be expected that the line can be sharply drawn between *mixtures* and *combinations* of cellulose with non-cellulose constituents of either fibres or tissues. Frémy (*Ann. Agronomiques*, 9, 529) recognises the existence of the following compounds distinguished from cellulose chiefly by their different behaviour to hydrolytic reagents and cuprammonia; (1) *Fibrose*, constituting the membranes of wood cells; (2) *Paracellulose*, constituting the membrane of the pith and medullary rays, and (3) *Vasculose* constituting the membranes of the vessels. The value of this somewhat arbitrary classification is questionable (Sachsse, *Farbstoffe, Kohlehydrate*, &c., p. 150), and the distinctions which it seeks to establish have not been generally recognised. On the other hand, there are certain groups of substances widely distributed throughout the plant world, which, while they have certain features in common with the celluloses, are sufficiently distinct to admit of chemical classification apart from them. Generally speaking, these substances are made up of a *cellulose* and a *non-cellulose* portion, the latter conferring the special features of distinction. The compound cellulose thus constituted is resolved, by treatment with reagents according to the methods to be described, into cellulose or a cellulose residue on the one hand, and soluble derivatives of the *non-cellulose* on the other. Of these groups we shall consider typical members.

The following are the compound celluloses sufficiently characterised to warrant special description under class names: the nomenclature of these compounds is explained by their characteristic resolutions.

Pectocelluloses

Resolved by hydrolysis (alkalis)
into
/ \
Pectic acid and cellulose.
Type: Raw flax
(Kolb, *Bull. Mulh.* 1868, *A. Ch.* [4] 14, 348).

Lignocelluloses

Resolved by chlorination
into
/ \
Chlorinated derivs.: Aromatic, Soluble in alkalis } and cellulose.
Type: Jute
(Cross a. Bevan, *C. J.* 41, 90).

Adipocelluloses

Resolved by oxidation
(Nitric acid)
into
/ \
Similar derivs.: as by the oxidation of the fats. } and cellulose.
Type: Cuticular tissue of leaves and fruits
(Frémy, *C. R.* 48, 667; Sachsse, *Farbstoffe*, &c.).

Pectocelluloses.—The purified bast of a Russian flax investigated by Kolb was found to have the aggregate composition:

C 43·7
H 5·9
O 50·4.

The non-cellulose constituent is therefore a substance of lower carbon percentage than cellulose. From its yielding pectic acid on boiling with alkalis, it is obviously a substance allied to pectin. Since the fibre yields about 20 p.c. of its weight of the acid derivative we infer independently that it is a substance containing approximately 41 p.c. carbon, which confirms the view of its constitution above expressed. Many other plant fibres are made up of or contain pectocelluloses (Webster, *C. J.* 43, 23); pectic derivatives were identified by Schunck in the products of the action of boiling alkaline solutions upon raw cotton (*Proc. Manchester Lit. Phil.* [3] vol. iv).

The cellular tissue of a large number of fruits, *e.g.*, the apple and pear, and roots, *e.g.*, turnips and carrots, is composed of pecto-celluloses.

Lignocelluloses.—The course of lignification in plants is marked by profound alterations in the physical properties of the tissues undergoing this modification; the tissues lose their elasticity, become coloured from grey to brown, and the substance of the tissues manifests the chemical properties about to be described.

Jute.—Aggregate percentage composition: C. 47·0–48·0, H. 5·9–5·7, O. 47·1–46·3 $(C_{12}H_{18}O_9)_n$. It may be regarded as composed of

Non-cellulose (Lignin) $C_{18}H_{24}O_{10}$ (55·5 p.c. C) 25 p.c.
and Cellulose $C_{18}H_{30}O_{15}$ (44·4 „) 75 „

though the cellulose isolated from the fibre by chemical resolution differs in composition as already stated from normal cellulose, appearing rather as an oxycellulose. The mineral constituents of the raw fibre (purified) vary from 0·5 to 2 p.c. of its weight; the hygroscopic moisture from 10–12. Attacked by concentrated solutions of the alkalis similarly to cotton; freely soluble in cuprammonia, but is incompletely precipitated on acidifying; the body remaining in solution gives the reactions of the original substance, and may, therefore, be regarded as a hydrated modification. Jute combines freely with the organic astringents (tannins) and the majority of aromatic colouring matters. It is coloured a bright yellow by solutions of salts of aniline and other aromatic bases. This reaction is probably due to a product of oxidation, since it does not take place with jute which has been boiled for some time in solutions of sulphites. It is coloured brown by iodine solutions. Moistened with a solution of phloroglucol and treated afterwards with hydrochloric acid it gives a deep red colouration; with pyrrol also in presence of hydrochloric acid it gives a deep carmine colour. A mixture of sulphuric and nitric acids nitrates the fibre, the gain in weight being approximately equal to that of cellulose under the same conditions. The products are orange-coloured and are soluble in acetone. Like the cellulose nitrates, they give no amido-derivatives on reduction. Iodine is absorbed by the fibre, the quantity taken up being constant under constant conditions; the resulting compound is not more stable than the iodide of starch. This

reaction may be made use of for the quantitative estimation of the lignocelluloses in cellulosic mixtures. Bromine attacks the fibre in presence of water, forming ill-defined compounds which are dissolved by alkaline solutions. The operation once or twice repeated eliminates the whole of the non-cellulose; the resulting cellulose amounts to 72–75 p.c. of the weight of the fibre. Chlorine does not act upon the dry fibre, even when the temperature is raised to 160°, but in presence of water combines rapidly at ordinary temperatures with evolution of heat. The chlorinated derivative is yellow coloured; it is soluble in alcohol, and from the solution water precipitates the compound $C_{19}H_{18}Cl_4O_9$, as a yellow flocculent mass. This compound gives a characteristic magenta colouration with sodium sulphite solution similar to that of mairogallol [1] (Webster, *C. J.* 45, 205). It dissolves in solutions of the caustic alkalis with a brown colour, evolving the characteristic odour of the chloroquinones. It yields chloropicrin on distillation with nitric acid. Fused with potassium hydrate it yields protocatechuic acid. It is therefore an aromatic derivative, and appears to be allied to the trihydric phenols. The chlorinated fibre when boiled with sodium sulphite solution is entirely resolved into cellulose, and soluble derivatives of the non-cellulose or lignin constituent. This constitutes the simplest and most rapid method of cellulose estimation in the fibre. The proportion of cellulose obtained is somewhat higher than by the bromine method (75–78 p.c.) and is further increased by preventing rise of temperature in the chlorination.

Digested with dilute nitric acid at 80° jute is resolved directly into cellulose (oxycellulose) oxalic and carbonic acids and a peculiar acid derivative of the lignin constituent. This body has the formula $C_{25}H_{16}(NO_2)O_{23}$; it is of an intense yellow colour, and dyes the animal fibres to a similar shade. It forms salts with the earthy bases ($C_{25}H_{32}(NO_2)O_{23}.M''_4$) which are precipitated by alcohol from aqueous solutions in the form of bright yellow flocks.[2]

Hydrolytic agents.—Jute and the lignocelluloses generally are much more susceptible of hydrolysis than the simple celluloses. The dilute acids effect a simple hydrolysis at 80°, *i.e.* the portion dissolved has the same composition and properties as the original; on raising the temperature to boiling, furfural is obtained in considerable quantity. Boiling dilute alkalis effect a simple hydrolysis. When the hydrolysis is complicated by the introduction of either reducing or oxidising conditions, resolution into cellulose and non-cellulose (soluble derivatives) is determined. Thus sulphurous acid, the bisulphites, and the normal sulphites (alkaline) attack and resolve the lignocelluloses when heated with their solutions under pressure. The temperatures necessary for efficient resolution, *i.e.* for the isolation of cellulose, are with sulphurous acid (7·5 p.c. SO_2) 90°–100°, with bisulphites (4 p.c. SO_2) 150°, with normal sulphites (4 p.c. SO_2) 170°–180°, the increase of temperature corresponding with the diminution of hydrolytic power by progressive neutralisation of the acid. The hydrolysis is aided by combination of the reagents with the soluble derivatives, which prevents the reversal of the action at the high temperature, which would otherwise occur. In heating with solutions of the caustic alkalis under pressure, a high temperature is necessary for complete resolution; a considerable proportion of the reagent is necessary for combining with the products, which under the oxidising conditions are of an acid nature. These facts are of importance in the preparation of cellulose from lignocelluloses, which is now a widely extended industry (*Forestry Exhibition Reports*, Edinburgh, 1885).

Animal Digestion.—It has long been known that the urine of the herbivora contains hippuric acid as a normal constituent, and it has been shown that the benzoyl radicle necessary to form this body is a product of the digestion of lignocellulose (Meissner). Since the lignocellulose molecule contains no aromatic compounds in the strict sense of the term (Stutzer, *B.* 8, 575) the process of digestion must effect the conversion.

Decomposition by Heat.—Cumulative Resolution. The celluloses burn in the air with a quiet luminous flame. When heated out of contact with the air they are completely resolved into gaseous and volatile products on the one hand, and a residual black mass, containing a high percentage of carbon. Regarding these carbonaceous substances as the products of condensation of cellulose molecules with elimination of water, the process may be viewed as, in the main, one of cumulative resolution by dehydration (Mills, *P. M.*, June, 1877); the cumulate containing hydrogen and oxygen in chemical union with carbon is still in every sense a compound; taking into consideration, at the same time, its approximation in appearance and properties to the element itself it may be termed a *pseudo-carbon*.[1] Dehydrating reagents effect similar resolutions, the lignocelluloses undergoing condensation more readily than the celluloses. The tendency to carbon accumulation which is the main feature of these resolutions is well marked in the vast series of natural products of the decay of cellulosic tissues, from humus to the coals. Though not of pyrogenic origin they nevertheless deserve mention in this connection from considerations of general resemblance.

It is noteworthy that the products of chlorinating ulmic substances (Sestini, *Gaz. It.* 1882, 292) are closely similar to those obtained from the lignocelluloses. Similar products are also yielded by the cannel coals.

Other forms of Lignocellulose. Two other varieties of lignocellulose deserve mention, viz. *glycolignose*, $C_{30}H_{46}O_{21}$, the substance of fir woods '*glycodrupose*,' $C_{30}H_{44}O_{20}$, the substance of the stony concretion of pears (Erdmann, *A.* 138, 1; *Suppl.* 5, 223; Bente, *B.* 8, 476; Sachsse, *Farbstoffe*, 151). On boiling with dilute

[1] According to Hantzsch a. Schniter (*B.* 20, 2033), mairogallol is a species of condensed quinone chloride—the characteristic molecule being derived from quinone by replacement of one of its typical O atoms by Cl_2, the aromatic linking being at the same time partially resolved. Such a view accords equally well with the properties of the derivative in question.

[2] It is worthy of note that the addition of urea to the dilute acid considerably modifies its action, which becomes one of simple hydrolysis as in the case of sulphuric and hydrochloric acids (*infra*).

[1] *Phil. Mag.*, 1882, 325.

hydrochloric acid these compounds are said to be resolved into a sugar and an insoluble residue, lignose $= C_{18}H_{26}O_{11}$, and drupose $= C_{18}H_{28}O_{12}$, respectively. On comparing these formulæ with those of the original substances, the differences are so slight as to be negligible. The action of the acid is probably therefore one of simple hydrolysis. The reactions of these substances are also in other respects identical with those of the jute substance. Although therefore differing from the ligno-cellulose, above described, in ultimate composition, they are essentially of the same order of compounds.

Crude fibre. This term is applied by agricultural chemists to the residual product of the treatment of fodder plants with boiling solutions of certain acids and alkalis, applied successively. The process is a crude imitation of the process of digestion in the animal, and the results which it yields are of purely empirical value. Crude fibre will be found on examination, in most cases, to be a ligno-cellulose and to be further resolved by chlorine in the manner indicated.

ADIPOCELLULOSES. *Cork and Cuticular Tissue.* From the mode of formation of these tissues it has been concluded, on physiological grounds, as in the case of the lignocelluloses, that they are modified celluloses (Sachsse, *Farbstoffe*, &c. p. 153). The ultimate composition of cork is represented by the following percentage numbers: C 65·7, H 8·3, N 1·5, O 24·5. Unlike the lignocelluloses, however, it is by no means a simple or homogeneous substance, but is resolved by the action of mere solvents into a number of proximate constituents, some of which are crystalline. The residue from the action of these solvents may be regarded as the true cork substance. It is resolved by the action of boiling nitric acid (20–30 p.c.) into cellulose on the one hand—only a small proportion (3–5 p.c.), however, surviving so severe a treatment—and a series of fatty acids (or products of their decomposition) such as suberic and adipic acids, on the other; the latter amount to about 40 p.c. of the weight of substance treated. If cork be resolved by treatment with sodium sulphite solution, at 166° a soft mass is obtained preserving the structural features of the original, but which on slight pressure breaks down into a cellular mass. On slight purification this yields a pure cellulose; the proportion obtained being from 9 to 12 p.c. of the original cork. From these resolutions into cellulose, and products of decomposition similar to those obtained from the fats and waxes under similar treatment, the substance of cork has come to be regarded as a compound of such molecules; and this view of its constitution, as well as that of the entire group of substances similar in composition and function, is summed up in the group term Adipocellulose, by which it is proposed to designate them. The cuticular tissues, such as constitute the covering of fleshy fruits and leaves, while similar in many respects, are simpler in composition. When purified they are non-nitrogenous and appear to be homogeneous.

Frémy and Urbain have developed (*C. R.* 100, 19) a somewhat different view of the constitution of these tissues. Taking the protective tissues of the leaf of the agave as the type, in addition to an interior epidermal layer, which is cellulosic, and is soluble in cuprammonia after treatment with boiling hydrochloric acid, they distinguish the external or true epidermis, which they term Cutose. The substance composing this tissue has the following properties: it is resolved by alkaline saponification into two fatty acids, *oleocutic* $C_{28}H_{40}O_4$ a liquid oily body, and *stearocutic* $C_{28}H_{48}O_4$, a solid body melting at 76°, soluble in benzene and glacial acetic acid, and slightly soluble in boiling alcohol, the solution gelatinising on cooling. The following numbers give the percentage composition of the original cutose and of the two derivatives.

	Cutose	*Oleocutic acid*	*Stearocutic acid*
C	68·4	66·6	75·5
H	8·7	8·2	10·3
O	22·9	25·2	14·2

Whence it is concluded that the molecule of cutose is composed proximately of oleo- and stearo-cutic acids in the molecular proportion of 5:1.

The two derived acids above described are marked by a curious instability or tendency to reversion, passing under certain conditions, notably by exposure of their solutions to light, into modifications closely resembling the original cutose.

With regard to the distribution of cutose in the plant world, while it is the main constituent of the external protective tissues of leaves, fleshy fruits and the stems of annuals, it is found also in the interior tissues, *e.g.* the bast and fibro-vascular bundles.

These researches are an important contribution to the subject; and while there is no reason to doubt the authors' conclusions in the main, it is probable that they have overlooked the presence of cellulose as a constituent of cutose which occurs as an organised *i.e.* cellular tissue. We need scarcely observe that the chemistry of these adipocelluloses has been but little investigated.

CONSTITUTION OF CELLULOSE.

The physical properties of cellulose throw but little light on the problem of its molecular constitution. We have seen, moreover, that cellulose is chemically inert; its derivative compounds are few, and of these indeed the nitrates alone appear to merit such a description, their formation being unattended by molecular resolution. From their composition and properties we infer the presence of alcoholic OH groups in the cellulose molecule. The gradual resolution by the action of sulphuric acid, through a series of compounds terminating with achroodextrin, indicates a certain constitutional relationship to the simpler carbohydrates of which the latter is a typical representative. The exact mechanism of the resolution not having been elucidated, it is impossible to draw any but the general inference from the products to the original cellulose molecule, viz., that the latter is a complex of molecules resembling these simpler and better known carbohydrates. We also infer that the bond which unites them is one of dehydration, but the exact nature of this bond is for the present entirely conjectural. (For a discussion of the probabilities involved in this problem the reader is referred to a paper by Baeyer entitled

'Wasserentziehung u. ihre Bedeutung für das Pflanzenleben und die Gährung,' *B.* 3, 63.) That such molecules are to be regarded physiologically as well as chemically, as the proximate constituents of the cellulose molecule, is a conclusion which has perhaps been somewhat prematurely drawn. Its ultimate origin is of course to be traced to the carbonic anhydride and water of the air and soil, the synthesising agencies being the protoplasm and chlorophyll of the plant, aided by the supplies of energy from without. It has been supposed that the mediate source of the vegetable carbohydrates is formic aldehyde, and the recent researches of Loew (*B.* 20, 141) upon the condensation of this aldehyde have at least confirmed the probability of this supposition. The products of resolution of cellulose, moreover, clearly indicate the presence of aldehydic groups in the molecules. Apart from conjecture, we may, to sum up this brief review, regard the cellulose molecule as a complex of simpler carbohydrate groups, containing alcoholic and aldehydic oxygen (*v.* also Bowman, *B. A.* 1887).

The most striking features of the empirical formula of cellulose $C_6H_{10}O_5$ are those characteristic of the entire group of carbohydrates, the molecule containing some multiple of C_6 and the hydrogen and oxygen having the ratio 2:1. At present these relationships are merely suggestive of conditions of molecular equilibrium to be elucidated by future investigation.

The prevalence of the C_6 group is remarkable and suggests a relationship to the aromatic group, which is confirmed by the undoubtedly cellulosic origin of the benzene compounds. On the other hand we have no evidence of the existence of closed chains of C atoms in the cellulose molecule, nor have any simple transitions from the one group to the other been as yet discovered. If we turn, however, from the typical cotton cellulose to other forms of cellulose, such as those isolated from growing tissues, we find in the ease with which many of them yield furfural as a product of acid hydrolysis, some evidence of a more complex union of the C atoms, than the normal type usually assumes. Passing on further to the lignocelluloses we find a molecule in the constitution of which a furfural group undoubtedly plays a part, and in which the linking of the C atoms is such as permits a simple transition, in part at least, to products of undoubtedly 'aromatic' composition.

We have, in this brief statement of the evidence which we have upon which to found our views of the constitution of cellulose, endeavoured rather to indicate the main lines upon which the investigation of the problems involved is proceeding, than to draw premature conclusions. The subject will be enormously developed in the future, and will constitute an important foundation of the natural history of the carbon compounds; a department of view of the science which can scarcely as yet be said to be within reach.

NOMENCLATURE.

Considerable confusion has been imported into this subject by the indiscriminate employment of the terms, cellulose, lignin, woody fibre, lignose, 'crude fibre,' in describing the various products, natural and artificial, of which this article treats. The want of uniformity arises from the division of the subject amongst physiologists, agriculturists and chemists. That which we have adopted appears to bring about a certain simplification.

The application of the term cellulose we have already defined and limited. To denominate the compound celluloses, which correspond with the chief modifications of cellulose recognised by physiologists, we use a compound term consisting of cellulose as the substantive portion with a qualifying prefix. To specially distinguish the characteristic constituent of these compounds, that to which we have applied the neutral term non-cellulose, we employ the root of the prefix with the termination *in*, thus *pectin*, *lignin*.

In conformity with this plan it may be expedient to introduce such terms as subero-cellulose, cuto-cellulose, suberin, cutin, and many others: but this should be left to be determined by the progress of investigation. The special classification and nomenclature proposed by Frémy has been already discussed. C. F. C.

CERASIN, the meta- acid (*v.* ARABIC ACID) existing in cherry-tree and plum-tree gums, and in the gums of other trees of the same family. Gum arabic yields cerasin when heated to 150° (Gélis, *C. R.* 44, 144). Cherry-tree gum is said to contain 52·1 p.c. arabin, 34·9 cerasin, 12 water, and 1 *ash*. Treated with nitric acid cerasin yield 15·5 p.c. mucic acid. C.O'S.

CERATIN *v.* PROTEIDS.

CERATOPHYLLIN. [147°]. Extracted by lime-water from the lichen *Parmelia ceratophylla* (Hesse, *A.* 119, 365). Thin prisms, sl. sol. cold, v. sol. hot, water; v. sol. alcohol, ether, and aqueous alkalis. Fe_2Cl_6 colours its alcoholic solution purple. Bleaching-powder gives a red colour.

CERBERIN. A poisonous, crystalline glucoside occurring in *Cerbera Odollam* (Oudemans, *J. pr.* 99, 407; de Vrij, *R. T. C.* 3, 167).

CEREBRIN C.69·08, H.11·47, N.2·13, O.17·32 (Parcus. From these numbers the formulæ $C_{70}H_{140}N_2O_{13}$; $C_{76}H_{154}N_2O_{14}$; or $C_{80}H_{160}N_2O_{15}$ may be calculated). The body called *Phrenosin* by Thudichum (*J. pr.* [2] 25, 19) is probably the same body in an impure state. The name cerebrin was used first by Kühn (1828) and applied to a mixture of cholesterin and lecithin. It was used by Lassaigne (1830) to denote the entire substance that can be extracted from brain by alcohol. It was employed by Gobley (1850) to denote so-called 'protagon;' and by Müller to denote the nitrogenous substance free from phosphorus that can be extracted from the brain by alcohol, to which he gave the formula $C_{17}H_{33}NO_3$.

References.—Fourcroy, *A. Ch.* 16, 282; Frémy, *J. Ph.* 27, 453; Liebreich, *A.* 134, 29; Gobley, *J. Ph.* [4] 19, 346; W. Müller, *A.* 103, 131; 105, 361.

Preparation.—Ox-brain is freed from membranes, washed with water, squeezed and heated with baryta to boiling. The clear liquid is poured off and the coagulated residue washed with nearly boiling water, dried and extracted with alcohol. The first extract deposits very

little on cooling, but cerebrin mixed with cholesterin separates from the subsequent extracts. The cholesterin is removed by solution in ether. So prepared, cerebrin is free from phosphorus but contains inorganic matter. 250 grms. were got from 90 brains. It is redissolved in alcohol at 60° which leaves a barium salt undissolved. The barium that goes into solution is removed by a current of CO_2. The cerebrin is purified by frequent recrystallisations from alcohol. The earlier mother-liquors deposit on standing a gelatinous pp. By recrystallisation from alcohol this pp. may be separated into cerebrin (spherical crystals), homocerebrin (needles), and encephalin (E. Parcus, *J. pr.* 132, 310).

Properties.—Separates as a white crystalline powder composed of transparent globules from a boiling alcoholic solution. Soluble in acetone, chloroform, benzene, and glacial acetic acid. Insoluble in ether. Separates from acetone partly as globules, partly as matted threads. Cerebrin dissolves in conc. H_2SO_4. On standing exposed to the air, the liquid becomes covered with a purple skin, which afterwards turns green. Cerebrin does not combine with acids, bases, or salts. It is not affected by boiling for a short time with baryta. It is but slightly decomposed by boiling alcoholic potash. Cerebrin swells up but slightly in boiling water. It is very slightly hygroscopic, absorbing 2 p.c. of water from the air. It is decomposed by boiling for a long time with baryta. Boiled for some hours with dilute HCl it forms a solution that can reduce Fehling's solution.

Homocerebrin C. 70·1 p.c. : H. 11·6 ; N. 2·2 ; O. 16·1. The yield is ¼ that of the cerebrin. Soluble in the same liquids as cerebrin ; soluble also in boiling ether. Swells up in hot water, but does not form a paste. Is not decomposed by boiling water. Treated with hot HCl, it forms a solution that reduces Fehling's solution. Boiled for a long time with baryta, it is decomposed. It is not hygroscopic. Its solutions are neutral. It does not combine with acids, bases, or salts. It separates from alcoholic solutions in very fine needles. After separation from alcohol and drying, it is not a white powder (like cerebrin) but a waxy mass. It is more soluble in absolute alcohol than cerebrin.

Encephalin. C. 68·4; H. 11·6; N. 3·1; O. 16·9. Resembles homocerebrin rather than cerebrin. It separates from solutions in flexible plates. From acetone it separates in granular masses. It swells up with hot water forming a complete paste. Boiled with HCl, it forms a solution that can reduce Fehling's solution.

CERIC ACID. C. 64·2 p.c.; H. 8·8 p.c.; O. 27·0 p.c. Obtained by the action of HNO_3 on cerin, or according to Kügler on phellonic acid $C_{22}H_{42}O_3$ [96°]. Phellonic acid is obtained, together with glycerin and stearic acid, by the action of alcoholic KHO on cork that has previously been exhausted by chloroform and alcohol (Döpping, *A.* 45, 289).

CERIN $C_{20}H_{32}O$(?). [250°]. A substance that may be extracted by chloroform from cork, the bark of *Quercus Suber*, in which it occurs to the extent of 2 p.c. (Kügler, *Ar. Ph.* [3] 22, 217; *cf.* Chevreul, *A. Ch.* 96, 170; Döpping, *A.* 45, 289). Needles, insol. water, sol. other solvents. According to Siewert (*Z.* 1868, 383) an alcoholic extract of cork contains **phellyl alcohol** $C_{17}H_{28}O$ [100°], a neutral, crystalline substance, sl. sol. alcohol.

CERIUM. Ce. At. w. 139·9. Mol. w. unknown as element has not been gasified. S.G. (abt. 18°) 6·63 to 6·73 (Hillebrand a. Norton, *P.* 156, 471). M.P. considerably above that of Sb (450°) but below that of Ag (950°) (H. a. N.). S.H. (0°–100°) ·04479 (H., *P.* 158, 7). S.V.S. 21·1. Chief lines in emission-spectrum 5352·2, 5273·2, 4628·2, 4572·6, 4562·1, 4296, 4289 (Thalén). In 1803 Klaproth, and independently Berzelius and Hisinger, separated a new earth from a Swedish mineral and called it *Ceria* (from the then recently discovered planet *Ceres*); in 1839-41 Mosander (*P.* 11, 406) proved that ceria was a mixture of at least three metallic oxides, oxides viz. of Ce, La, and Di. The metal cerium was first obtained by Mosander in 1826, it was more fully examined by Wöhler, Bunsen, and other chemists.

Occurrence.—In many Swedish minerals, more especially in *cerite* a silicate of Ce (abt. 56 p.c. Ce_2O_3); occurs as silicate, phosphate, carbonate, fluoride, &c., also in many *apatites*; generally accompanied by La, Di, Fe, Al, &c. It has been recently found that clay used for brickmaking at Hanistadt (near Seeligenstadt in the neighbourhood of Frankfurt) contains from 8 to 12 p.c. of Ce_2O_3 (Strohecker, *J. pr.* [2] 33, 133 a. 260).

Preparation.—Cerite is heated to redness, powdered, mixed with considerable excess of conc. H_2SO_4, and the mixture is gradually heated to incipient redness in a Hessian crucible; after cooling, the mass is powdered and then added, little by little, to ice-cold water, whereby sulphates of Ce, La, and Di are dissolved; the treatment with H_2SO_4 &c. is repeated with the portion insoluble in cold water; the aqueous solution is heated to boiling, whereby basic sulphates are ppd.; solution in ice-cold water and ppn. by heating to boiling are repeated several times (Marignac; Bunsen; Wöhler). The solution in cold water is ppd. by addition of oxalic acid solution; the oxalates are washed with water, dried, and heated in a Pt dish until completely converted into oxides. The mixed oxides (of Ce, La, and Di) may now be treated in many different ways. The following method was used by Brauner (*C. J.* 47, 884) in order to prepare pure Ce_23SO_4 for atomic weight determinations; it is based upon the formation of basic Ce nitrate insoluble in water. The mixed oxides were dissolved in moderately conc. HNO_3Aq, excess of acid was removed by evaporation, and the syrup-like liquid was poured into much *pure* boiling water ; the ppd. basic ceric nitrate was washed (on a funnel connected with a pump) with boiling water containing a little nitric acid. The nitrate was dissolved in HNO_3Aq, excess of acid was removed by evaporation, the liquid was poured into boiling water, &c., as already described. This treatment was repeated 10 or 11 times. From the pure basic ceric nitrate thus obtained other Ce compounds may be prepared. Brauner prepared Ce_23SO_4 by dissolving the basic nitrate in dilute H_2SO_4Aq, and H_2SO_4Aq, evaporating to dryness in a Pt dish, and heating with due precaution, dissolving in a little ice-cold water, ppg. by absolute alcohol, washing

with abs. alcohol, dissolving in ice-cold water, ppg. by alcohol, dissolving again, heating to 100° and stirring with a glass rod; $Ce_2 3SO_4.6H_2O$ was thus obtained; it was dehydrated by heating for some weeks at 440° in molten sulphur; at full redness the sulphate gives off SO_2 and SO_3 and leaves pure CeO_2.

Robinson (*Pr.* 37, 150) prepared pure Ce_2Cl_6. The mixed oxides from cerite were dissolved in HNO_3Aq (*v. supra*), and the liquid, after concentration to a syrup, was poured into boiling dilute H_2SO_4Aq; the basic sulphates were dissolved in HNO_3Aq, the Ce salt oxidised by boiling with PbO_2 (Gibbs, *Am. S.* [2] 37, 352), the liquid evaporated, and La and Di salts removed by treatment with HNO_3Aq; the pure basic ceric nitrate remaining was converted into chloride by treatment with KClAq, from this Ce oxalate was obtained by ppn. with oxalic acid; the oxalate was heated in dry HCl, and pure Ce_2Cl_6 was thus obtained (for details *v.* original). Robinson (*l.c.*) also recommends evaporating the nitric acid solution of the mixed nitrates to complete dryness, heating the brown mass to full redness until the residue is pale-yellow, and treating this with boiling dilute HNO_3Aq; Ce basic nitrate remains while nitrates of Di and La dissolve.

Other methods for preparing more or less pure Ce salts are described by Bunsen, *P.* 155, 375; Czudnowicz, *J. pr.* 80, 16; Watts, *C. J.* 2, 147; Holtzmann, *J.* 1862. 136; Jolin, *Bl.* [2] 21, 533; Erk, *Z.* [2] 7, 100; Popp, *A.* 131, 361; Pattison a. Clark, *C. N.* 16, 259. Wöhler (*A.* 144, 251) prepared Ce by adding pieces of Na to a molten mixture of Ce_2Cl_6, KCl, and NH_4Cl; the product, however, was impure. Hillebrand a. Norton (*P.* 155, 633; 156, 466) by electrolysing Ce_2Cl_6, covered with NH_4Cl, using a thick iron wire as negative electrode (4 Bunsen's cells) obtained approximately pure cerium. (For details *v.* original papers.)

Properties and Reactions.—Steel-grey, very lustrous, very ductile, metal; malleable, unchanged in dry air, but in moist air is superficially oxidised; heated in air burns to oxide with production of heat and much light; burns in Cl, Br, I vapour, S vapour, P vapour, forming compounds with these elements; easily dissolved by HClAq, dilute HNO_3 or H_2SO_4Aq, no reaction with cold conc. HNO_3 or H_2SO_4Aq. Ce slowly decomposes cold water, quickly decomposes hot water. As the V.D. of no Ce compound has yet been determined, the At. w. of the metal must be fixed by chemical considerations and by S.H. The value given to the At. w. for many years was abt. 92, and the formulæ of the oxides, and chloride, &c., were CeO, Ce_2O_3, $CeCl_2$, &c.; Ce was thus placed, along with La and Di, in the same class as Al and the earth metals. Considering the relations between the properties of compounds of Ce, La, Di, and of other elements, Mendelejeff (*A. Suppl.* 8, 186) thought that Ce ought to be classed with those elements which form well-marked oxides MO_2, *i.e.* with Ti, Zr, Sn, &c. If this were done the At. w. of Ce would become $92 \times \frac{3}{2}$. Further investigation has completely justified Mendelejeff's proposal; Ce is now classed with C, Si, Ti, Zr, Sn, Pb, and Th; La is placed with Al and the earth metals, and Di is classed with the elements of Group V. whose characteristic highest oxide is M_2O_5.

The At. w. of cerium has been determined (1) by estimating SO_3 in cerous sulphate (Beringer, *A.* 42, 134; Rammelsberg, *P.* 55, 65; Hermann, *J. pr.* 30, 184; Marignac, *A. Ch.* [3] 27, 209; 38, 148). (2) by estimating Cl in cerous chloride (Beringer, *l.c.*; Robinson, *Pr.* 37, 150). (3) from combustions of cerous oxalate (Jogel, *A.* 105, 45; Rammelsberg, *P.* 108, 44). (4) by conversion of $Ce_2 3SO_4$ into CeO_2 by heat (Brauner, *C. J.* 47, 879). (5) by determining S.H. of approximately pure Ce (Hillebrand a. Norton, *P.* 156, 471). The most accurate determinations are those made by Robinson and Brauner, respectively: both lead to the number 139·90 (O = 15·96).

Cerium is distinctly metallic in its physical and chemical properties; it forms the oxides Ce_2O_3 and CeO_2 (and probably also CeO_3), both of these are salt-forming in their reactions with acids, but the well-marked salts (cerous salts) are those corresponding to Ce_2O_3, *e.g.* $Ce_2 3SO_4$ &c.; in this respect Ce differs from Ti, Zr, Th, Sn, and Pb, the salts of which metals belong to the forms MX and MX_2(X = SO_4, CO_3, $2NO_3$, &c.); and shows analogies with the elements of Group III. (Al &c.). Ce does, however, form a ceric sulphate $Ce2SO_4$; besides the oxide CeO_2, a fluoride CeF_4 analogous to TiF_4, ZrF_4, &c., is known (*v.* CARBON GROUP OF ELEMENTS; also TITANIUM GROUP OF ELEMENTS.)

Detection and Estimation.—Ce salts are generally soluble in water: alkalis pp. white hydrated Ce_2O_3; NaClOAq pps. yellow hydrated CeO_2 which dissolves in HClAq in presence of alcohol to form a colourless liquid; solutions of Ce salts are ppd. by oxalic acid, the ppd. oxalate is white and insoluble in NH_4 salts; saturated K_2SO_4Aq pps. a white crystalline double sulphate, scarcely soluble in cold water, decomposed and dissolved by hot water containing a little HCl; Ce salts boiled with PbO_2 and a little HNO_3Aq give a yellow solution. When a slightly acid solution of a Ce salt is mixed with ammonium acetate, a little H_2O_2Aq is added, and the whole is warmed, a yellowish pp. is formed (Hartley, *C. J.* 41, 202); if this pp. is moistened with NH_3Aq, again treated with H_2O_2Aq, and warmed, an orange solid (? CeO_3) is produced (de Boisbaudran, *C. R.* 100, 605). Ce can be separated from La and Di only by very prolonged treatment, *v. Preparation.* Ce is usually estimated as CeO_2, but it is very difficult to obtain this oxide pure. For methods of separation and estimation a manual of analysis must be consulted.

Cerium, carbide of. Said to be obtained as a dense black powder, insoluble in hot conc. acids, by heating cerous formate or oxalate in a stream of H, and treating with HClAq to dissolve out any oxide formed. Analyses agree approximately with composition CeC_6 (Delafontaine, *J.* 1865. 177).

Cerium, haloid and oxyhaloid compounds of. Cerium forms cerous haloid compounds, Ce_2X_6 or CeX_3, corresponding to the oxide Ce_2O_3; and also a ceric fluoride CeF_4: the molecular weight of none of these compounds has been determined.

Cerous bromide. Ce_2Br_6 or $CeBr_3$. Known as the hydrate $CeBr_3.xH_2O$. Obtained by dissolving cerous oxide, Ce_2O_3, in HBrAq and evaporating. Deliquescent needles; unchanged by heating out of contact with air; heated in air, partially decomposed with loss of Br. Forms double salt $CeBr_3.AuBr_3.8H_2O$ (Jolin, *Bl.* [2] 21, 323).

Cerous chloride. Ce_2Cl_6 or $CeCl_3$. Obtained by heating Ce in Cl; or by dissolving Ce_2O_3 in HClAq, adding NH_4Cl, evaporating to dryness, and driving off NH_4Cl by heating; or by passing a mixture of dry CO and Cl over hot Ce_2O_3 (Didier, *C. R.* 101, 882). Pure $CeCl_3$ was prepared by Robinson (*Pr.* 37, 150) by heating pure $Ce_2(C_2O_4)_3$ in pure dry HCl gas to 120°–130° for some time, then to 200°, and then to low redness; the small quantity of C separated was removed by heating at low redness in mixed CO_2 and HCl; finally the temperature was raised to a full red heat and the CO_2 stream was stopped. The chloride was allowed to cool in HCl gas, transferred to a small flask, and kept *in vacuo*, over H_2SO_4 and surrounded by CaO, until all HCl was removed. S.G. $\frac{15°}{15°}$ 3·88 (Robinson, *l.c.*). A white, deliquescent solid; easily soluble in water with production of heat; decomposed by O, or by steam, to Ce_2O_3 (Didier). A hydrate, $CeCl_3.7H_2O$, is said to be formed by digesting Ce_2O_3 in HClAq and evaporating. Various double salts are described; *e.g.* $CeCl_3.4HgCl_2.10H_2O$, $CeCl_3.PtCl_4.13H_2O$, $CeCl_3.AuCl_3.13H_2O$ (Jolin, *l.c.*).

Cerous cyanide (and *double cyanides*) *v.* Cyanides.

Cerous fluoride. CeF_3 obtained as a gelatinous pp. ($2CeF_3H_2O$) by adding NaFAq to $CeCl_3$ in HClAq (Jolin).

Ceric fluoride. CeF_4H_2O. An amorphous brown powder, insoluble in water, obtained by treating $CeO_2.6H_2O$ with HFAq, washing, and drying at 100°. Decomposed by heat with loss of H_2O and HF and formation of CeF_3; heated strongly in contact with moist air CeO_2 and HF are formed. Combines with KF (by treatment with KF.HF) to form $2CeF_4.3KF.2H_2O$ (Brauner, *C. J.* 41, 69).

Cerous iodide. Ce_2I_6 or CeI_3. Obtained as the hydrate $CeI_3.9H_2O$, in colourless crystals, by dissolving Ce_2O_3 in HIAq, evaporating in a current of H_2S, and placing *in vacuo* over H_2SO_4: soluble in water and alcohol, very quickly decomposes in air (Lange, *J. pr.* 82, 134).

Cerium oxychlorides. The compound $Ce_4O_3Cl_6$ ($=Ce_2O_3.2CeCl_3$) is said to be formed when $CeCl_3$ is heated with Na (in preparation of Ce) and the mass is treated with water. Dark purple, lustrous, powder; insoluble in water (Wöhler, *A.* 144, 254). The same oxychloride is said to be obtained, as iridescent scales, by passing a mixture of steam and N over a fused mixture of $CeCl_3$ and NaCl; easily soluble in dilute acids; heated in air gives Ce_2O_3 and HCl (Didier, *C. R.* 101, 882).

Cerium, hydroxides of, *v.* Cerium, oxides of.

Cerium, oxides and hydrated oxides of. The best studied oxides are cerous oxide Ce_2O_3, and ceric oxide CeO_2; a peroxide CeO_3 also probably exists. Other oxides, *e.g.* Ce_2O_5 and Ce_4O_9, have been described, but their existence is very doubtful.

Cerous oxide. Ce_2O_3. (*Cerium sesquioxide.*) Mol. w. unknown. The white, bulky pp. obtained by adding KOHAq to a solution of a cerous salt is hydrated cerous oxide; as the pp. at once begins to take up O and CO_2 from the air the hydrate has not yet been obtained pure. The oxide Ce_2O_3 is prepared by heating cerous oxalate in a stream of pure H. The oxalate is prepared from the basic nitrate (*v.* Cerium, *Preparation*) by dissolving in a little HNO_3Aq and ppg. by oxalic acid (Popp, *A.* 131, 361; Rammelsberg, *B.* 6, 86).

Properties and Reactions.—A grey solid; unchanged by heating in H. Dissolves in many acids to form cerous salts of the form Ce_2X_3, $X=SO_4$, CO_3, $2NO_3$, $2ClO_4$, &c.

Ceric oxide. CeO_2. (*Cerium dioxide*). The pale yellow pp. obtained by suspending $Ce_2O_3.xH_2O$ in KOHAq and passing in Cl is hydrated ceric oxide ($2CeO_2.3H_2O$; Rammelsberg, *P.* 108, 40).

Formation.—1. By washing the hydrate with water containing a little acetic acid until KOH is removed, drying and heating.—2. By heating cerous sulphate Ce_23SO_4 to full redness in air. 3. By heating CeF_4 in air (Brauner).

Preparation.—Cerous oxalate is prepared from the basic nitrate from *cerite* (*v.* Cerium, *Preparation*); it is heated to redness in a Pt dish with free access of air. Nordenskiöld (*P.* 114, 616) obtained colourless, transparent, several crystals of CeO_2 by heating CeO_2 for 24 hours with a little borax in a porcelain oven, and treating the mass with HClAq: S.G. at 15° = 6·94.

Properties and Reactions.—Very pale yellow solid (Wolf, Brauner, Robinson [*C. N.* 54], Crookes, *Pr.* 38, 414). S.G. 6·74 (Nilson a. Pettersson, *B.* 13, 1159). S.V.S. 25·45. S.H. ·0877 (N. a. P., *Pr.* 31, 46). Dissolves in conc. H_2SO_4Aq with production of much heat, and evolution of some O; on crystallising, the salt $Ce_23SO_4.Ce(SO_4)_2.24H_2O$ separates (Mendelejeff, *A.* 168, 45); from the mother-liquor of this salt ceric sulphate $Ce2SO_4.4H_2O$ is obtained. This reaction shows that part of the CeO_2 is reduced by the H_2SO_4 to Ce_2O_3, and part reacts with the acid to form $Ce2SO_4$. Dissolves in HNO_3Aq; on adding NH_4NO_3 and crystallising *in vacuo* the double salt $2Ce(NO_3)_4.4NH_4NO_3.3H_2O$ is obtained. Scarcely soluble in HClAq; but dissolves in this acid, and also in other dilute acids, in presence of reducing bodies, *e.g.* filter-paper, alcohol, SO_2Aq, &c.

Cerium trioxide. CeO_3. (*Cerium peroxide.*) Said to be obtained as a reddish pp. by adding a slight excess of NH_3Aq to Ce_23SO_4Aq, and digesting with hydrogen peroxide (de Boisbaudran, *C. R.* 100, 605; Cleve, *Bl.* [2] 43, 53).

Other oxides of cerium are described by Popp (*A.* 131, 361); Hermann (*J. pr.* 30, 184; 82, 385; 92, 113); the formulæ Ce_4O_9 and Ce_2O_5 are assigned to these oxides, respectively; but experiments made by Rammelsberg (*P.* 108, 40) and others tend to show that the only oxides which have been isolated are Ce_2O_3, CeO_2, and CeO_3.

Cerium, oxychlorides of, *v.* under Cerium, haloid and oxyhaloid compounds of.

Cerium, salts of.—Salts obtained by replacing H of acids by Ce. Two series of salts are known, cerous salts represented by $Ce_2 3SO_4$, and ceric salts represented by $Ce2SO_4$. The cerous salts correspond to the oxide Ce_2O_3, the general form of these salts is Ce_2X_3 where $X = SO_4$, CO_3, $2NO_3$, $2ClO_4$, &c.; the ceric salts correspond to the oxide CeO_2, their general form is CeX_2 where $X = SO_4$ &c. The cerous salts are considerably more stable than the ceric salts; the latter are readily reduced to the former; but few ceric salts have been obtained, the principal salt is $Ce2SO_4$; several double salts are known of the form $Ce2SO_4.xM_2SO_4$, and $Ce4NO_3.xMNO_3$, when M is an alkali metal. Many double cerous salts are known. A few basic salts are also known. Some salts have been isolated which appear to belong to the mixed form $xCe_2X_3.yCeX_2$; and one of the so-called basic nitrates is probably $xCe_26NO_3.yCeO_2$. For descriptions of the individual salts *v.* the articles on the various groups of salts, CARBONATES, SULPHATES, &c.; the chief salts are the *bromate, carbonates, iodate, nitrates, oxalate, perchlorate, phosphates, selenate, sulphates, tungstate.*

Cerium silicide. Described by Ullik (*Z.* [2] 2, 60) as a brown powder; obtained by passing an electric current from 8 Bunsen-cells through a fused mixture of KF and Ce_2F_6 in a porcelain crucible, and treating with water the brownish mass formed at the negative pole. The Si was derived from the crucible which was strongly attacked. Analysis gave numbers nearly agreeing with the formula Ce_2Si_3.

Cerium, sulphides of. Only one sulphide is known, cerous sulphide, Ce_2S_3. It is best obtained by passing dry H_2S over CeO_2 heated to full redness in a porcelain tube. S.G. 5·1. Vermilion to black according to the temperature at which prepared. May also be obtained in red translucent crystals by passing dry H_2S over a fused mixture of dry NaCl and dry Ce_2Cl_6, and then washing with water. Unchanged in ordinary air; but burnt to SO_2 and CeO_2 below a red heat in air. Dissolves easily in dilute acids with production of H_2S; very slowly decomposed by warm water (Didier, *C. R.* 100, 1461; *v.* also Lange, *J. pr.* 82, 129; and Mosander, *P.* 11, 406).

Cerium, sulphocyanide of; *v.* SULPHOCYANIDES, under CYANIDES. M. M. P. M.

CEROPIC ACID $C_{36}H_{68}O_5$ (?) In the leaves of the Scotch fir (*Pinus sylvestris*), from which it may be extracted by dilute alcohol. Minute needles.—BaA″ aq (Kawalier, *A.* 88, 360).

CEROSIN $C_{24}H_{48}O$. [82°]. A waxy substance found on the stem of the sugar-cane. Nacreous laminæ (from alcohol). Heating with potash-lime oxidises it to cerosic acid $C_{48}H_{96}O_3$ (?) [93°], which may be crystallised from petroleum (Avequin, *A. Ch.* 75, 218; Dumas, *A. Ch.* 75, 222; Lewy, *A. Ch.* [3] 13, 438).

CEROTENE $C_{27}H_{54}$. [58°]. A product of the distillation of Chinese wax (Brodie, *P. M.* [3] 33, 378; *A.* 67, 210). Resembles paraffin. Chlorine forms $C_{27}H_{36}Cl_{18}$, $C_{27}H_{33}Cl_{21}$, and $C_{27}H_{32}Cl_{22}$. A similar body [66°] occurs in hay; it is perhaps $C_{20}H_{42}$ (König a. Kiesoff, *B.* 6, 500).

CEROTIC ACID $C_{27}H_{54}O_2$ or $C_{26}H_{52}O_2$. [78°].

Occurrence.—1. As ceryl cerotate in Chinese wax; whence it is obtained by distillation, or, better, by treatment with alcoholic KOH.—2. In the free state in bee's wax (John, *Chemische Schriften*, 4, 38; Boudet a. Boissenot, *J. Ph.* 13, 38; Ettling, *A.* 2, 267; Hess, *A.* 27, 3; Gerhardt, *Rev. scient.* 19, 5; Lewy, *A. Ch.* [3] 13, 438; Brodie, *A.* 67, 180; Zatzek, *M.* 3, 677).

Formation.—By oxidation of paraffin with dilute HNO_3 or with chromic mixture (Gill a. Meusel, *C. J.* 21, 466). Also by heating ceryl alcohol with soda-lime (Schwalb, *A.* 235, 141).

Preparation.—The alcoholic extract from bee's wax is recrystallised till it melts at 70°. This is dissolved in alcohol and the lead salt thrown down by alcoholic lead or cupric acetate.

Salts.—NaA′.—CuA′$_2$ at 100°.—PbA′$_2$ [113°].—KA′.—MgA′$_2$? [140°-145°].—AgA′.

Methyl ether MeA′. [60°] (Nafzger, *A.* 224, 233).

Ethyl ether EtA′. [60°]. Fatty plates (from alcohol). Soluble in ether. May be distilled *in vacuo*. On distillation it gives off C_2H_4 and CO_2 and the distillate contains cerotic acid and a paraffin [44°] ($C_{26}H_{54}$ or $C_{27}H_{56}$) while in the retort there remains a ketone [92°] which is $(C_{25}H_{51})_2CO$ or $(C_{26}H_{53})_2CO$.

Ceryl ether $C_{27}H_{55}.O.C_{27}H_{53}O$. [82°] Occurs almost pure as Chinese wax (Brodie) Occurs also in opium-wax (Hesse, *B.* 3, 638) and in yolk, the sweat of sheep (Buisine, *Bl.* [2] 42, 201).

An acid [79°] isomeric or identical with cerotic acid is the chief acid present in the product of saponification of carnaüba wax. From alcohol it separates as a jelly, but from other solvents (ether, benzene, light petroleum) as a crystalline powder (Stürcke, *A.* 223, 283; *cf.* Bérard, *Z.* [2] 6, 465).

Salt.—PbA′$_2$ [118°]. Sol. boiling glacial acetic acid and toluene. Insol. boiling alcohol or ether.

CEROTONE $C_{53}H_{106}O$ *i.e.* $(C_{26}H_{53})_2CO$ (?) [62°]. Formed by distilling lead cerotate (Brückner, *J. pr.* 57, 17). Plates (from ether).

Cerotone $(C_{26}H_{53})_2CO$ (?) [92°]. Formed by distilling cerotic acid or its ethyl ether (Nafzger, *A.* 224, 237). Plates (from acetone).

CERYL ALCOHOL $C_{27}H_{56}O$ or $C_{26}H_{52}O_2$. [79°].

Occurrence.—Chinese-wax consists almost entirely of ceryl cerotate (Brodie, *A.* 67, 180; Schwalb, *A.* 235, 141). Ceryl cerotate also occurs in the sweat on the wool of sheep. The wax outside ripe heads of the opium poppy contains ceryl cerotate and ceryl palmitate, [79°] (Hesse, *B.* 3, 637).

Preparation.—Chinese-wax is saponified with alcoholic potash, the product mixed with baric chloride solution and the ceryl alcohol separated from baric cerotate by solution in alcohol.

Reactions.—Is oxidised to cerotic acid $C_{27}H_{54}O_2$ by heating with soda-lime.

Iso-ceryl alcohol $C_{27}H_{56}O$. [62°]. The portion of the wax of *Ficus gummiflua* which is insoluble in cold ether (Kessel, *B.* 11, 2113).

Acetyl derivative $C_{27}H_{55}OAc$. [57°].

CESPITINE $C_5H_{13}N$(?). (95°). Occurs in coal tar, and in the product of the distillation of peat (Church a. Owen, *P. M.* [4] 20, 110; Fritzsche, *J.* 1868, 402). Liquid, miscible with water. Combines with EtI. Its platinochloride is de-

composed by boiling water (De Coninck, *Bl.* [2] 45, 131). Goldschmidt a. Constam (*B.* 16, 2978) suggest that it is wet pyridine.

CETANE *v.* HEXADECANE.

CETENE $C_{16}H_{32}$ *i.e.* $CH_3.(CH_2)_{13}.CH:CH_2$. *Cetylene. Hexadecylene.* [4°]. (275°); (155°) at 15 mm. S.G. $\frac{4}{4}$ ·7917; $\frac{15}{4}$ ·7842. V.D. 8·0. Formed by distilling cetyl alcohol with P_2O_5 (Dumas a. Péligot, *A. Ch.* [2] 62, 4; Smith, *A. Ch.* [3] 6, 40). Also by distilling cetyl palmitate or commercial spermaceti (*cf.* Krafft, *B.* 16, 3018). Oil; sol. alcohol and ether. According to Berthelot (*A. Ch.* [3] 51, 81) it forms unstable compounds with HBr and HCl. It forms a dibromide $C_{16}H_{32}Br_2$ [14°] whence alcoholic KOH forms oily bromo-cetene (Chydenius, *A.* 143, 267). HClO forms chloro-cetyl alcohol $C_{16}H_{32}Cl(OH)$ (c. 300°) (Carius, *A.* 126, 195). SO_3 forms $C_{16}H_{31}SO_3H$ [18°], insol. water.—KA': [106°]; S. 1 (Lasarenko, *B.* 7, 125).

An isomeride of cetene, [42°], (284°) is got by distilling azelaic acid with baryta (Schorlemmer, *A.* 136, 265).

CETENE GLYCOL. The *di-acetyl derivative* $C_{16}H_{32}(OAc)_2$ is formed by the action of AgOAc on cetene dibromide. It cannot be distilled (Chydenius, *A.* 143, 270).

CETENE OXIDE $C_{16}H_{32}O$. [below 30°]. (below 300°). From chloro-cetyl alcohol (*v.* CETENE) and aqueous KOH (Carius, *A.* 126, 202). Minute needles.

CETIC ACID $C_{15}H_{30}O_2$. [55°]. The glyceryl derivative occurs in the oil expressed from the seeds of *Jatropha Curcas* (Bouis, *J.* 1854, 462). According to Heintz (*P.* 90, 137) a very small quantity of this acid is found in the products of saponification of spermaceti.

Ethyl ether EtA'. [21°] (P.).

CETINENE $C_{16}H_{30}$. *Cetylene. Hexadecinene. Hexadecylidene.* [20°]. (284°). (160°) at 15 mm. S.G. $\frac{20}{4}$ = ·804; $\frac{30}{4}$ = ·797. H.F. 118,000 (Berthelot). Large colourless tables. Formed by heating cetene (hexadecylene) bromide (natural or synthetical) with alcoholic KOH (Krafft, *B.* 17, 1373; *cf.* Chydenius, *C. R.* 64, 180).

CETRARIC ACID $C_{18}H_{16}O_8$. Contained, together with lichenostearic acid, in Iceland moss (*Cetraria islandica*) (Berzelius, *Schw. J.* 7, 317; *A. Ch.* 90, 277; Herberger, *A.* 21, 137; Knop a. Schnedermann, *A.* 55, 144). Hair-like needles (from alcohol), v. sl. sol. water, sl. sol. ether, v. sol. boiling alcohol. Tastes bitter. Decomposed before melting. Its solutions turn brown on boiling, especially in presence of alkali. Fe_2Cl_6 gives a red pp. in neutral solutions.—$(NH_4)_2A''$.—PbA''.

DICETYL $C_{32}H_{66}$. *Dotriacontane.* [70°]. (above 360°). V.D. 15·8. Formed by treating an ethereal solution of cetyl iodide with sodium (Sorabji, *C. J.* 47, 37; *cf.* Lebedeff, *J. R.* 1884, [2] 299). Scales, v. sl. sol. ether, v. sol. boiling glacial HOAc.

CETYL ACETATE $C_{16}H_{33}OAc$. *n-Prim-hexadecyl acetate.* [19°] (Becker, *A.* 102, 220); [23°] (Krafft, *B.* 16, 1721). (278°) at 190 mm.; (200°) at 15 mm. (K.). S.G. $\frac{15}{15}$ ·8640; $\frac{25}{25}$ ·8612. M.M. 18·772 at 20·7° (Perkin, *C. J.* 45, 421). Needles; sl. sol. cold alcohol.

CETYL-ACETIC ACID is identical with STEARIC ACID (*q.v.*).

Di-cetyl-acetic acid $C_{34}H_{68}O_2$ *i.e.* $(C_{16}H_{33})_2CH.CO_2H$. [70°]. Formed by heating di-cetyl-malonic acid at 150° (Guthzeit, *A.* 206, 365). Crystalline scales, sl. sol. alcohol.—AgA': amorphous pp.

CETYL ALCOHOL $C_{16}H_{34}O$. *Æthal. n-Prim-hexadecyl alcohol.* Mol. w. 242. [50°]. (344°); (190°) at 15 mm. S.G. (liquid) $\frac{50}{4}$ = ·8176; $\frac{60}{4}$ = ·8105; $\frac{99}{4}$ = ·7837. H.F. 112,000 (Berthelot).

Occurrence.—Spermaceti is cetyl palmitate $(C_{16}H_{33})C_{16}H_{31}O_2$ (Chevreul, *Recherches sur les corps gras*, p. 171; Dumas a. Péligot, *A. Ch.* [2] 62, 4; Dumas a. Stas, *A. Ch.* [2] 73, 124; Smith, *A. Ch.* [3] 6, 40; *A.* 42, 247; Heintz, *P.* 84, 232; 87, 553). In the sebaceous glands of geese and ducks (De Jonge, *H.* 3, 225).

Formation.—By the distillation of baric sebacate (Schorlemmer, *Pr.* 19, 22).

Preparation.—1. Spermaceti (10 pts.) is boiled with alcohol (5 pts.) and potash (2 pts.) until saponified. The product is poured into water and the cetyl alcohol crystallised from ether. The crude commercial cetyl alcohol contains in addition to hexadecyl alcohol also *n-p*-octadecyl alcohol and probably small quantities of other homologues (Krafft, *B.* 17, 1627).—2. The acetate is formed by reducing palmitic aldehyde (obtained by distilling barium palmitate with barium formate) with zinc-dust and acetic acid (Krafft, *B.* 16, 1721).

Properties.—Small crystalline plates (from alcohol). Gives palmitic acid on oxidation.

Sodium Cetylate $C_{16}H_{33}NaO$. [110°] (Fridau, *A.* 83, 1).

Ethyl ether $C_{16}H_{33}OEt$. [20°] (Becker, *A.* 102, 220).

TRI-CETYL-AMINE $C_{48}H_{99}N$ *i.e.* $(C_{16}H_{33})_3N$. [39°]. From cetyl iodide and gaseous NH_3 at 150° (Fridau, *A.* 83, 25). Needles. Its salts are insol. water, sol. alcohol and ether.—B'HCl.—$(B'HCl)_2PtCl_4$: yellow pp.

CETYL-ANILINE $C_{22}H_{39}N$ *i.e.* $N(C_6H_5)(C_{16}H_{33})H$. *Phenyl-cetyl-amine.* [42°]. From cetyl iodide and aniline at 100° (Fridau, *A.* 83, 29). Silvery scales (from alcohol). Has no action on litmus, and does not pp. metallic salts. $B'_2H_2PtCl_6$.

Di-cetyl-aniline $N(C_6H_5)(C_{16}H_{33})_2$. From cetyl-aniline and cetyl iodide at 110° (F.). Crystalline.—$B'_2H_2PtCl_6$.

CETYL-BENZENE $C_6H_5(C_{16}H_{33})$. *Hexadecyl-benzene.* [27°]. (230° at 15 mm.) Formed by the action of sodium upon a mixture of iodo-benzene and cetyl iodide (Krafft, *B.* 19, 2983).

CETYL-BENZENE-SULPHONIC ACID $C_6H_4(C_{16}H_{33}).SO_3H$. *Hexadecyl-benzene-sulphonic acid.* Formed by sulphonating cetyl-benzene. The sodium salt A'Na is sparingly soluble (Krafft, *B.* 19, 2983).

CETYL BENZOATE $C_{16}H_{33}OBz$. [30°] (Becker, *A.* 102, 219). Crystalline scales.

CETYL BORATE $C_{16}H_{33}BO_2$. [58°] (Schiff, *A. Suppl.* 5, 198).

CETYL BROMIDE $C_{16}H_{33}Br$. [15°]. From cetyl alcohol, Br, and P (Fridau, *A.* 83, 15). Insol. water, v. sol. alcohol and ether.

CETYL CHLORIDE $C_{16}H_{33}Cl$. S.G. $\frac{12}{}$ ·841. From cetyl alcohol and PCl_5. Oil, insol. alcohol, sol. ether. Boils above 280° with decomposition (Dumas a. Péligot, *A. Ch.* 69, 4; Tüttscheff, *Rép. Chim. pure*, 2, 463).

CHEMICAL AND PHYSICAL PROPERTIES OF BODIES, CONNEXIONS BETWEEN. Certain properties are common to all kinds of matter, others are characteristic of this or that kind only. Thus, every material substance is acted on by the force of gravity in exactly the same manner, but only a few liquids rotate the plane of polarisation of a ray of light. Properties belonging to the second of these classes are subdivided into two groups, physical and chemical properties. Chemistry deals with those changes in the properties of material bodies which are accompanied by changes in the composition of the bodies. Physics deals with changes in the properties of bodies the composition of which remains the same. When the totality of properties by which a body is known remains unaltered throughout any process, that process is called physical; when the result of any process is a body or bodies with properties so different from the totality of those of the original that the original can no longer be said to exist, that process is called chemical. Physical and chemical processes are always closely connected in their occurrence; no chemical change takes place without some accompanying physical change, and it is probable that every physical change is to some extent accompanied by chemical change. Many physical properties are quantities which may be accurately measured; *e.g.* melting- and boiling-points, specific gravity, &c., &c. Change of composition of a body or system of bodies is very frequently accompanied by change in the value of one or more of these measurable quantities; in other words, the physical constants of a body are conditioned, among other circumstances, by changes in the variable, chemical composition. By the chemical composition of any homogeneous kind of matter is meant, in the first place, a statement of the elements, and of the mass of each element, in a given mass of that body: in this meaning of the term the chemical composition of a body or system can be accurately stated, and definite relations can be determined between changes in the composition and changes in the values of such physical properties as melting- and boiling-points, specific rotatory power, specific refractive energy, and so forth. When the relations between the two groups of changes have been studied and generalised, it may become possible to infer the amount and character of a change of composition from measurements of the changes in the values of a few physical properties. It would be impossible to study the relations between every chemical change and the accompanying variations in the physical properties of the bodies forming the changing system; it is necessary to select typical cases, and to study these as accurately and minutely as possible. As a rule, one physical property is chosen for measurement; the composition of the system is defined to begin with; the system is allowed, or caused, to pass into another definite state; and the variation in the value of the chosen property is determined.

But when it is found that several distinct kinds of matter exist, each homogeneous, each distinguished by definite properties, and each containing in a given mass the same masses of the same elements, it becomes necessary to widen the meaning of the expression chemical composition. It becomes necessary to frame an hypothesis to account for the observed facts The hypothesis generally adopted asserts that matter has a grained structure, that a mass of any kind of homogeneous matter is composed of a vast but not indefinite number of minute parts; and that the properties of the mass are conditioned by the properties of these parts. These minute portions of matter are called molecules. But the molecule is not necessarily itself without parts. The chemist asserts that every molecule is built up of a definite number of smaller parts either of one or of several kinds of matter. These parts of molecules are called atoms. The atoms of elements are the ultimate forms of matter with which chemistry at present concerns itself. The hypothesis goes on to assert that the properties of a molecule, and hence the properties of any portion of homogeneous matter composed of molecules of this kind, are conditioned by the nature, the number, and the relative arrangement, of the atoms which together form the molecule. In other words, the hypothesis declares that the molecule is itself a structure. On this hypothesis, by the chemical composition of a body is meant a statement of the nature, number, and relative arrangement, of the atoms which form a molecule of the body. We know as yet almost nothing about the configuration of atoms in molecules; but chemistry has formed certain more or less clear hypotheses, and attempts are constantly being made to connect changes in the values of various physical properties with variations in the relative arrangement of atoms in molecules, as this arrangement is conceived by the hypotheses in question.

But the physical conception of the molecule is derived from the study of various gaseous phenomena: the physicist deals with the molecule as a whole; he pictures the molecules as performing certain vibrations, on the form, amplitude, and rate, of which the physical properties of bodies depend. The two conceptions, the chemical and the physical conception, of the molecule are therefore to a great extent mutually independent. In how far then, one may ask, can a development of the chemical conception be looked for by using physical methods of inquiry? Looking at recent researches, it seems probable that the chemical conception of the molecule must be very considerably modified, and must be brought more into harmony with the physical conception. The latter is itself to some extent being changed by the development of the theory of vortex atoms. But it must not be forgotten that the physical conception, in so far as it is a clear conception, has been developed almost wholly from the study of gaseous laws, more especially of the laws which express the relations of the volumes of gases to temperature and pressure; these relations are independent on the states of combination of the parts of molecules, and are in no way affected by the nature or number of these parts. The chemical conception, on the other hand, must be made sufficiently elastic to cover the phenomena presented by gaseous,

liquid, and solid, compounds; and most of the chemical processes which occur among compounds belonging to these classes are conditioned both by the nature and number, and by the states of combination of the atoms which form the chemical molecules of the reacting bodies. The chemical conception of the molecule will probably be modified when we know more of those properties which, like the relation between the volumes of gases and the temperature and pressure of these gases, are to a great extent, if not altogether, independent of the nature and numbers of the constituent parts of molecules. The physical conception will probably be modified as we learn more of those properties which, like specific heat, are for the most part dependent on the nature and numbers of the constituent parts of molecules. (*v.* MOLECULAR STRUCTURE OF MATTER, THEORIES REGARDING).

Chemistry regards not only changes in the composition, but also changes in the properties, of bodies; she attempts to generalise not only the laws of composition, but also those of the mutual actions, of bodies. The study of the connexions between changes of composition and variations in physical properties of chemically reacting bodies will throw light on the nature of chemical change. When accurate measurements have been made of the quantities of heat which disappear or are produced in a series of typical chemical processes we shall be able to apply to these processes the knowledge of heat-energy which is generalised in the thermodynamical laws. Chemical change may then perhaps be shown to be a special instance of the working of these laws. The conditions of chemical change on the one hand, and of physical change on the other, must be studied, in order that the laws which express these conditions may be gained; the relations between these two groups of laws must then be ascertained; thus it may become possible to attain to clear mental images of natural phenomena as wholes which now present one aspect to the physicist and another to the chemist.

For accounts of the various physical methods employed in chemistry, and résumés of the more important results, *v.* PHYSICAL METHODS.

M. M. P. M.

CHEMICAL CHANGE. Chemical science is based upon the hypothesis that matter is constituted of extremely small particles or atoms, and that these atoms are capable of aggregating together by virtue of certain inherent properties or forces, their affinities, to form complex atomic structures or groupings.

The recognition of this distinctive force by the older chemists led them to propound various theories to account for its existence and explain the phenomena of chemical action (*v.* AFFINITY).

With the nature of this force we are not concerned here, but only with the phenomena that accompany its exhibition and the circumstances that modify its action.

By a chemical change, therefore, is meant any alteration either (1) of the character of a permutation in an atomic group, such for instance as is exhibited in the change of ammonium cyanate, NH_4CNO, into urea $(NH_2)_2CO$; or (2) a permutation between two or more such groups, as $AB + CD = AD + BC$, which groups may be of various degrees of complexity; or (3) the change may arise from a combination such as $AB + CD = ABCD$, or the converse of this, as is seen in the phenomena of dissociation.

The majority of chemical changes may be formulated as permutations between two sets of atomic groups; such as the action of bases on acids, the decomposition of one salt by another, or the combination between gaseous elements as $H_2 + Cl_2 = 2HCl$. Examples of chemical change according to case (3) are of less frequent occurrence than the last; such are the formation of double salts like the alums, the combination of certain gaseous molecules with oxides, &c., as $CaO + CO_2 = CaCO_3$ and $CO + Cl_2 = COCl_2$. The number of strikingly marked instances that could come under the head of permutations in an atomic group is very small, but such changes may be of frequent occurrence, producing alterations in physical and chemical properties too slight to be recognisable.

There are several bodies which are known to undergo remarkable and highly interesting physical, and consequently no doubt chemical, changes, when heated, but whether such changes come under class (1) or class (3) is undecided. Among such substances are phosphorus, paracyanogen, and cyanuric acid. In the case of phosphorus, the change from the yellow to the red modification, caused by heat or light, is probably due to an alteration in the state of aggregation of the atoms; that is to say, if the molecule of yellow phosphorus be P_n that of the red modification is probably P_m; for solid paracyanogen, which is converted by heat into gaseous cyanogen, and for cyanuric acid, the same may be true, with or without a re-arrangement among the constituent atoms of the molecules (*v.* ALLOTROPY and ISOMERISM).

The study of the phenomena attending a chemical change shows that in many instances there is an accompanying evolution of energy, from the changing system, in one form or other, either as heat, or light, or as electrical currents. In other cases to produce a chemical change expenditure of energy is necessary.

What may be the nature of the chemical force or affinity that acts between atoms is not known, but it is characterised from gravitative force by this difference, that whereas gravitation acts upon all kinds of matter alike, depending merely on the masses of the bodies, chemical attraction or affinity depends upon the kinds of matter that are presented to each other, as well as upon the conditions under which the bodies are brought together; in other words, it is an elective attraction modifiable by circumstances. For instance, at a red heat metallic iron is oxidised by water vapour and hydrogen is set at liberty, but at a lower temperature oxide of iron is reduced by hydrogen with the formation of metallic iron and water vapour; a mixture of hydrogen and chlorine will remain unchanged for any length of time in darkness, but exposure to sunlight will cause almost instantaneous combination, and the resulting compound (hydric chloride) may be again converted into its original constituents by heat. If to a solution of silver nitrate a piece of metallic copper be added, metallic silver is ppd., and copper nitrate formed; and if now to the

copper nitrate a piece of zinc or iron be added, metallic copper is ppd., and zinc or iron nitrate is formed.

These illustrations are sufficient to show the relativity of chemical affinity as depending both upon the conditions to which the system is subjected as well as upon the qualities of the materials.

Under whatever conditions a chemical system may exist in which a change is happening, the atomic forces at work will continue to act until a state of more or less stable equilibrium is reached, after which no further action will take place; and the ultimate limit reached will depend upon (1) the relative quantities of the reacting bodies; and (2) the conditions to which the system is subjected. As the system passes from the initial to the final configuration there will be a loss or gain of energy equal in amount to the difference between the total energy of the system in the two states. The rate at which the change takes place will depend also upon the same two circumstances. These two statements amount to this; that, representing a chemical change by the equation $A+B=A'+B'$, all the atomic forces at work producing the transformation have not invariably the same ratios, but that the ratios vary with variations in the conditions as regards heat, light, &c.; and, consequently, any determinations of the relative affinities of the members of the system can only be looked upon as expressing certain ratios that hold good under special conditions. The final state reached by the system, and the rate at which the change progresses towards that state, vary with the relative masses of the reacting bodies, other things being equal, although the atomic forces or the affinities remain the same. In other words the final configuration, and the speed of attaining it, are each a function of the reacting masses and of the atomic forces, the latter being a function of the physical conditions to which the system is subjected.

The phenomena of dissociation furnish many examples of these facts; as do also those systems which are limited by inverse actions and do not properly come under the term dissociation, wherein both the masses of the constituents as well as the conditions, especially as regards heat, influence the change in its amount and rate. The great field offered for investigation by fractional pptn. will, no doubt, afford many striking instances of the variations of the affinity values under diverse circumstances when the subject is worked out.

From the foregoing considerations it is clear that a chemical system may or may not undergo change by virtue of any intrinsic forces acting among the constituents, but that such will happen only according to the conditions to which it is subjected. Reactions which at moderate temperatures take place with evolution of much energy may be completely suspended by lowering or increasing the temperature, excluding light, or altering the pressure; in other words, the forces or affinities resisting change, if greater than those tending to produce an alteration under some circumstances, may be reversed when these circumstances are altered.

There are, however, a number of interesting examples in which the stability of a system seems to be overturned by the mere presence of an extraneous body which itself undergoes no apparent change. For instance, oxygen and SO_2 do not combine when moderately heated, but if passed over spongy platinum combination readily occurs. Sometimes again the intermediate body does undergo change, as when chlorine is passed over a strongly heated mixture of carbon and silica, whereas without the addition of carbon the silica is not acted upon by the chlorine; or, platinum, which itself is insoluble in nitric acid, may be rendered soluble in the same acid by alloying it with silver (*v. post*, Catalytic changes, p. 750).

Some equally remarkable instances of the apparent necessity of the presence of a third body in order to bring about chemical action between two others have been noticed. Wanklyn (*C. N.* 20, 271) found that perfectly dry chlorine gas has no action upon metallic sodium. Couper (*C. J.* 43, 153), starting from Wanklyn's observation, has examined the action of dry chlorine on several metals that are acted upon vigorously by the moist gas. He found that dry chlorine has no perceptible action on Dutch metal, whereas with the moist gas combination takes place, with production of heat and light; or on touching the metallic surface when in an atmosphere of dry chlorine with a drop of water, instant combination occurs. Couper examined a number of metals in the same way with the following results: the chlorine gas used was allowed to stand over $CaCl_2$ for several days to thoroughly dry it. Zinc, and magnesium, showed no action; silver, slight action; bismuth, combination slow; arsenic, antimony, and tin, rapidly acted upon. It is worthy of note that these last three metals form volatile chlorides liquid at ordinary temperatures. With mercury, combination equally rapid, with dry or moist chlorine. Potassium showed slight action, probably due to adhering KHO; with proper precautions against moisture, action was slow. Dixon (*T.* 1881, 617) has observed a somewhat analogous fact relating to the combination of gases under the influence of the electric spark. He has shown that if a mixture of CO and O be perfectly dried by P_2O_5, and be then subjected to the spark from a large Leyden jar or a Ruhmkorff's coil, union does not take place; if, however, the slightest trace of moisture be admitted to the mixture, and the spark again made to pass, combination occurs. The hypothesis Dixon advances to account for these facts is that the intervention of water molecules is necessary to bring about combination, a molecule of water being decomposed under the influence of the spark by one of carbonic oxide to form carbonic acid and free hydrogen, the latter in its turn combining with the oxygen to form water: this cycle of operations being represented by the equations $H_2O+CO=H_2+CO_2$; $H_2+O=H_2O$; consequently a comparatively small number of water molecules are necessary to effect complete combustion. (See also *C. J.* 49, 94.) Phosphorus and carbon have been shown by Baker (*C. J.* 47, 349) to combine with oxygen less energetically in the absence of moisture, than when moisture is present; and Ramsay and Young (*C. J.* 45, 93) observed that if a mixture of dry H and N is passed through a tube containing iron filings at a red heat no

ammonia is formed; with the moist gases, however, a trace of NH_3 is obtained.

Allotropic Change.

Several of the elementary bodies are known to exist in two or more different modifications, such for instance as sulphur, selenion, carbon, phosphorus, and oxygen; the several forms of each element exhibit more or less strongly marked differences in chemical as well as physical properties. It is probable that such different modifications of one elementary body consist, as in the case of oxygen and ozone, of different atomic groupings or aggregates of atoms. The means by which the change from one modification of an element to another is brought about are various. Oxygen is converted into ozone by the electric spark or 'silent discharge,' and ozone is changed again into oxygen by heat; yellow phosphorus is converted into the red modification either by light or by heat, and the red modification is again reconverted into yellow phosphorus at a higher temperature; sulphur and selenion undergo several changes under the influence of heat; in the case of carbon, the conditions necessary to bring about metamorphoses are not fully known.

The study of certain isomeric compound bodies (*v.* Isomerism) has shown that the transformation of one isomeride into another is, in some cases, somewhat analogous to the phenomena of dissociation. If solid paracyanogen $(CN)_n$ is heated in a closed vessel to 860° it is entirely converted into cyanogen gas $(CN)_2$; the pressure increases until the gas condenses and is liquefied on the cooler parts of the apparatus. At temperatures below 500° little or no decomposition occurs. As the paracyanogen is heated above this temperature a slow transformation takes place into gaseous cyanogen, and the transformation continues until the pressure of the cyanogen gas attains a certain definite limit beyond which it does not rise, and there is no further evolution of gas. Exhausting the apparatus and maintaining the temperature, the pressure again rises to its previous limit and remains stationary however long the heating is continued. For every such temperature there is a maximum pressure reached which limits the further decomposition of the paracyanogen into gaseous cyanogen. If now when the pressure has attained its limit, at a given temperature, a quantity of cyanogen gas is forced into the apparatus, the pressure slowly falls to the initial limit with the transformation of gaseous cyanogen into solid paracyanogen. Troost a. Hautefeuille (*C. R.* 66, 735, 795) have found the following values for these pressures of transformation at different temperatures:—

Temp.	Pressure of transformation.
502°	54° mm.
506	56 „
559	123 „
575	129 „
587	157 „
599	275 „
601	318 „
629	868 „
640	1310 „

The transformation of solid paracyanogen into gaseous cyanogen is seen to be analogous to the volatilisation of a liquid in presence of its own vapour; but the formation of red phosphorus from the yellow material or *vice-versâ* is a more complex process. If a quantity of yellow phosphorus is heated in a closed vessel (say to 500°), the mass of phosphorus being more than sufficient to volatilise in the space, a maximum pressure is quickly attained. After a time the pressure gradually falls, more or less quickly according to the temperature, till it reaches a minimum at which it remains constant. Provided there is no change of temperature, the vapour of the phosphorus is gradually converted into the red modification which condenses on the sides of the apparatus. If the quantity of phosphorus introduced into the apparatus is just sufficient to volatilise and fill the vessel with vapour at the first pressure (the heating being continued), red phosphorus begins to form after a time, and the pressure continues to fall until the minimum limit is reached as before. If, however, only sufficient ordinary phosphorus is used to fill the apparatus with vapour at the lower limit of pressure, no red phosphorus is formed, however long the heating may be continued. These two pressures the maximum is first attained, and the final minimum limiting the transformation of yellow into red phosphorus—depend solely upon the temperature. Troost and Hautefeuille (*A. Ch.* [5] 2, 153) found the following numbers relating to these phenomena:

Temp.	Pressure of vapour of P limiting the transformation	Maximum pressure of P vapour first produced
360°	·12 atms.	3·2 atms.
440	1·75 „	7·5 „
487	6·80 „	—
494	—	18 „
503	—	21·9 „
510	10·8 „	—
511	—	26·2 „
531	16 „	—
550	31 „	—
577	56 „	—

The rates at which the transformation takes place as well as other phenomena exhibited during the change have been studied by Lemoine (*A. Ch.* [4] 24, 194). He gives the following numbers illustrative of the progress of the change in time:

Ordinary P per litre. Grams.	Quantities of ordinary P remaining at 440°, after							
	mins.	¾ h.	2h.	8h.	17h.	24h.	32h.	4[illegible]h.
2·9	—	—	—	2.9	—	—	—	—
5·9	—	—	—	5·3	—	—	4·9	4·7
16·0	—	—	—	5·0	—	—	—	—
24·0 (Hittorf)	5·5	11·1	7·0	4·4	—	—	—	—
30·5	—	—	5·4	4·0	3·7	3·6	—	—

Lemoine (*C. R.* 73, 990) has given a mathematical theory of the changes that red or yellow phosphorus undergoes when heated in a closed vessel, and has compared his formulæ with the results of experiment. Let P be the total mass

of material introduced into a space V, and let y be the mass of yellow phosphorus formed or existing at time t; if the red phosphorus be supposed to remain in the same state of division throughout, its free surface will be sensibly proportional to its mass $P-y$. The quantity of yellow phosphorus evolved, δy_1, in time δt is equal to $a(P-y)\,\delta t$, and the quantity of the ordinary phosphorus, δy_2, transformed into the red modification in the same time is $b(P-y)\frac{y}{V}\,\delta t$; the total effect is therefore the difference between these two quantities, or

$$dy = \delta y_1 - \delta y_2 = a(P-y) - b(P-y)\frac{y}{V}$$

which may be written $\frac{dy}{dt} = f(g-y)\,(h-y)$, representing the rate of change in terms of the ordinary phosphorus existing.

For further account of Allotropic Changes *v.* ALLOTROPY.

INFLUENCE OF PRESSURE ON GASEOUS CHANGES.

Many bodies when subjected to the influence of heat in the gaseous state, undergo marked changes either in their physical or chemical properties, or in both; such changes result more particularly in a diminution of molecular density or a disruption of molecular structure. Among such bodies may be cited, mercurous chloride, chloral hydrate, phosphoric chloride, hydriodic acid, nitric peroxide, hydric selenide, amylic bromide, and acetic acid. In the case of some of these bodies the changes in question have been proved to be the accompaniment of disruption or dissociation of their molecules (*v.* DISSOCIATION); in other cases, such as nitric peroxide and acetic acid, there is no complete proof that the changes in density which these bodies suffer when heated in the gaseous state are really occasioned by a dissociation of their molecules, or are due to the fact of their vapours not obeying the dilatation-law even when sufficiently far removed from the liquid state as to place them under the category of gases. Considered from these two points of view, it is evident that the dilatation of a gas under the influence of heat may be of a twofold character, arising from two distinctly separate causes; firstly, the expansion may be purely physical, varying or not according to the dilatation-law, and secondly, there may be expansion as the accompaniment of a chemical change, viz., separation of the gaseous molecules into simpler groups of atoms. An observed variation of density at different temperatures may be produced by either of these two causes, or by both combined, and it becomes therefore a matter of great importance to be able if possible to discriminate these two actions, and to say to which of them the observed results are to be ascribed. If it could be shown that a diminution of pressure produced the same variation in the densities of certain gases as has been observed under the influence of heat, a great point would be gained in favour of the dissociation-theory in settling the cases under dispute. It would seem possible that a discrimination between the two possible phenomena accounting for abnormal densities might be made by introducing the element of time into such investigations. To make this clear, take the gas *nitrogen tetroxide*, whose vapour density at low temperatures has been found to be approximately represented by the formula N_2O_4, while at high temperatures it corresponds to NO_2 (the vapour densities being 3·18 and 1·59 respectively). Now Troost (*C. R.* 86, 1394) found the vapour density of nitrogen tetroxide at 27° and at low pressures to be as follows:

Pressure.	Density.
35 mm.	1·6
16 „	1·59 (NO_2 = 1·59).

These results show that the same change takes place under diminished pressure as occurs under the influence of heat at ordinary atmospheric pressures; that is to say, these numbers indicate that, if the observed changes in density are due to dissociation of the molecules N_2O_4 into the molecules NO_2, then under a pressure p the ratio of the number of molecules of N_2O_4 to NO_2 is different from the ratio when the pressure is altered to p', temperature being the same in each case. The proof of this assertion is of considerable importance in the theory of dissociation; whether the change in density is or is not to be attributed to the supposed fact, that the gas N_2O_4 forms an exception to the dilatation-law, would seem to be capable of indisputable proof by introducing the element of time into the experiments. If the gas N_2O_4 is really dissociated into NO_2 under diminished pressure, 2 vols. N_2O_4 would give 4 vols. NO_2; now, by the kinetic theory of gases it is conceivable that this dissociation would take place practically instantaneously when the temperature was increased or the pressure was diminished, whereas on reversing the process the molecules of NO_2 would require some time before meeting with the requisite number of partners to re-form the molecules of N_2O_4. Such an experiment might form a crucial test of the truth of the dissociation-hypothesis for this particular gas, and it might also be applied to other cases, for it is scarcely conceivable that the coefficient of dilatation of a gas should alter in time. Natanson (*W.* 24, 454) has determined the ratio between the specific heats of nitrogen tetroxide by means of Kundt's dust-figure method; his results seem to show that as the pressure decreases this gas passes from a more to a less complex molecular structure.

In the determination of the vapour densities of several bodies whose abnormal dilatations are almost undoubtedly to be ascribed to the disruption or dissociation of their molecular structures, the influence of time on the phenomenon has been several times observed, and has been made the subject of investigation by Naumann for the particular case of ammonium carbamate (*v.* next page).

Wurtz (*C. R.* 60, 728), when determining the vapour density of amylic bromide (B.P. 113°) between 153° and 360°, noticed that when the vapour was suddenly heated to 225° the density was 4·69, whereas in another experiment when the vapour had been maintained at this temperature for ten minutes the density was 3·68. These results show undoubtedly that the diminution in density, or the dissociation produced by heating, required time to be effected, and hence was

due to a chemical change and not to a variation in the coefficient of dilatation of the gas.

Naumann (*A.* 160, 1) studied the influence of time on the dissociation and re-formation of ammonium carbamate; the following tables illustrate the general bearing of his experiments:—

Speed of dissociation of $(NH_3)_2CO_2$ at 46°.

Pressure under the dissociation-pressure, which =354 mm.	Increase of pressure	Time of increase
129 mm.	—	—
37	87 mm.	5 min.
17	20	5
10	7	5
6	4	5
4	2	5
3	1	5
2·5	·5	5
2	·5	5
1·5	·4	5
0	1·5	17

Speed of formation a combination of $2NH_3 + CO_2$) at 20°.

Excess of pressure over dissociating-pressure (=62·4 mm.) at 20°	Decrease of pressure	Time of decrease
185 mm.	—	—
140 „	45 mm.	2·5 mins.
90 „	50 „	5 „
63 „	27 „	5 „
45 „	18 „	5 „
30 „	15 „	5 „
21 „	9 „	5 „
15 „	6 „	5 „
10 „	5 „	5 „
6 „	4 „	5 „
4 „	2 „	5 „
1 „	3 „	10 „
0 „	1 „	5 „
0 „	0 „	5 „

In these two examples it is seen that, starting with a mass of solid ammonium carbamate (Naumann showed by his experiments that at all temperatures the gas evolved consists of $2NH_3 + CO_2$) and suddenly increasing the temperature, a considerable time is required before the normal pressure of dissociation corresponding to that temperature is reached. In like manner, by suddenly diminishing the temperature, the recombination of the ammonia with the carbon dioxide to form the solid $(NH_3)_2CO_2$ does not take place instantaneously, but a considerable time elapses before the pressure corresponding to the lower temperature is arrived at. Although analogous in some respects to the volatilisation and condensation of a liquid, the phenomena exhibited by $(NH_3)_2CO_2$ when heated are characterised by their greater slowness.

In experiments relating to vapours of varying densities—such as those of Troost on acetic acid and nitric tetroxide at low pressures—it is important to determine whether diminution of pressure acts in a manner similar to that of heat in bringing about dissociation, or disruption, of the molecules of the gas. By introducing the element of time into the experiments, and by suddenly varying the pressure, dissociation might be shown to occur in the case of nitric tetroxide as already remarked, the process in this case being doubtless reversible; whereas with say, ozone, or a mixture of ozone and oxygen, the amount of change produced by increasing the volume, say, twenty-fold, could be determined by the usual methods of analysis (*cf.* also DISSOCIATION, and EQUILIBRIUM, CHEMICAL).

CHEMICAL SYSTEMS.

Considering the three physical states in which bodies are capable of undergoing chemical change, either as gases, liquids, or solids, it is evident that there are two distinct kinds or classes of chemical systems possible, according to the states in which the active substances exist, and which may be termed heterogeneous and homogeneous systems. The former name is applied to all reactions in which the active members of the system are in different physical states, a solid and a liquid, or a solid and a gas, or a liquid and a gas; as examples of each of these may be mentioned the action of acids on metals or on carbonates, the dissociation of calcic carbonate or ammonic carbamate by heat, and the oxidising action of free oxygen on solutions of stannous or ferrous salts. By homogeneous systems are to be understood those in which all the active members exist in the same physical state, either as liquids or gases; it is inconceivable that two solid bodies, however finely powdered and well mixed, could come under this category. Examples of homogeneous systems are shown in the numerous etherification processes, the oxidising action of potassic chlorate on ferrous salts, the action of oxalic acid on potassic permanganate, among liquids, and for gaseous systems, the action of iodine or selenion on hydrogen, and the influence of light on a mixture of chlorine and hydrogen or on gaseous hydriodic acid. Many valuable facts have been brought out by the study of heterogeneous chemical systems, especially as regards dissociation-phenomena; but the great field in which the most fundamental facts concerning chemical action will be gathered is naturally that embracing homogeneous systems, for here the most intimate contact exists among the acting substances, affording free play to the various chemical forces at work, and the secondary physical changes which interfere with the primary chemical change are reduced to a minimum.

Heterogeneous Systems.—Gladstone and Tribe (*Pr.* 19, 498) have investigated the rate at which a more positive metal immersed in a solution of a salt of a less positive one displaces the latter, and the relation which exists between the rate of action and the mass of salt in the solution. Employing a solution of argentic nitrate, the displacing metal being copper, and allowing the action to continue for ten minutes under varying conditions of concentration, they found that by doubling the amount of silver salt in solution the amount of action that took place during this interval of time was trebled. Zinc and cupric chloride, zinc and cupric sulphate, zinc and lead nitrate, iron and cupric sulphate,

and other combinations, showed in every case, when the solutions were sufficiently diluted, that this 2–3 law holds good. Expressed algebraically, if y be the mass of metal dissolved, and x the concentration of the solution, then the above 2–3 law is $y=ax^{\log\frac{3}{2}}$ where a is a constant.

These experiments have been repeated and extended by Langley (*C. J.* 45, 663), who confirms the truth of Gladstone's law; but when the method of experimenting is modified, as by continually moving the metal about in the solution or by brushing its surface so as to keep the solution uniform throughout, Langley considers that the rate of action is proportional solely to the amount of salt in solution. Moreover, Langley's experiments indicate that the law observed by Gladstone and Tribe arises from two causes, viz., chemical action, and gravitative action, the latter producing slow currents through the solution because of the changing densities of the original salts and of those which are produced in the change.

In studying the rate of evolution of carbon dioxide from marble by the action of acids, Bojuski and Kajander (*B.* 10, 34) found that the rate of action is proportional to the concentration of the acid, but varies according to the nature of the acid employed; moreover, they concluded that, for the three acids HCl, HBr, and HNO_3, the speed of the action is inversely proportional to the molecular weights of the acids when the solutions are of equal degrees of concentration. Pawlewski (*B.* 13, 334) has continued these experiments, employing different carbonates ($BaCO_3$, $CaCO_3$, $SrCO_3$) with the same acid; although his results are not very regular, yet he considers them sufficient to show that the speed of the reaction is inversely proportional, not to the molecular weights of the carbonates, but to the atomic weights of the metals whose carbonates were employed.

Of a somewhat similar nature to the experiments of Gladstone and Tribe is the work of Thorpe (*C. J.* 41, 287) on the behaviour of zinc, magnesium, and iron, as reducing agents, with acidulated solutions of ferric sulphate. Known weights of these three metals in the form of thin foil were introduced into acidified solutions of ferric sulphate, and the amount of reduction effected—part of the liberated hydrogen coming off as gas—under varying conditions of temperature, amount of free acid, and strength of the ferric solution, was determined. The results obtained showed that the reduction effected when a given mass of zinc dissolves in an acidified solution of ferric sulphate increases with increase of temperature, other conditions being the same. Provided a sufficiency of acid to dissolve the zinc be present, the maximum reducing action is obtained by concentrating the ferric sulphate solution, and diminishing the amount of free acid.

When magnesium is employed the reduction effected is scarcely one-fourth of that for zinc, while the time required for solution is comparatively very short; by diminishing the quantity of free acid the amount of reduction effected is increased. The diminution in the rate of solution with a decrease in the quantity of free acid was found to be much greater in the case of magnesium than in that of zinc; with zinc the rates were approximately in the ratios 1:1·5:2, and, under like conditions with magnesium, the rates were as 1:6:36. When the ferric sulphate is reduced by iron, the rate of solution becomes extremely slow, and the reducing action appears to decrease with increase of temperature. These reduction-experiments, considered as a whole, seem to be in harmony with the view that the reducing action of so-called nascent hydrogen is connected with the existence of atoms, as distinguished from molecules of this gas; and that any conditions which tend to prevent the mutual combination of these atoms tend also to increase the amount of reduction effected by the hydrogen.

When phosphorus oxychloride acts upon certain nitrates, it has been found that the ratio between the chlorine and phosphoric pentoxide in the residue obtained after all action has ceased has a certain definite value. Mills (*P.M.* [4] 40, 134, and 44, 506), who has studied this reaction for several nitrates, has designated these ratios by the symbol a, or rather he has taken a as $=\dfrac{\dfrac{\text{weight of chlorine}}{Cl}}{\dfrac{\text{weight of } P_2O_5}{P_2O_5}}$ $=\dfrac{\text{weight of Cl}}{\text{weight of } P_2O_5}\cdot 4·06$. When one nitrate fixes more chlorine, per unit of P_2O_5, than another nitrate, Mill says that the affinity of the former is greater than that of the latter nitrate; inasmuch as this chlorine-fixing action can be measured for several nitrates, the values of a, on Mill's view, represent the 'elective attractions' of the nitrates.

If a be divided by the formula-weights, Σ, of the several nitrates, calculated to a uniform mass of NO_3, the following numbers (under Q) are obtained:—

	a	Σ	Q
Thallous nitrate	8·78	265·30	30·29
Silver "	5·48	169·94	31·01
Lead "	5·17	165·56	32·02
Rubidium "	2·38	147·40	61·93
Cæsium "	2·21	195·01	88·24
Potassium "	1·99	101·14	50·82
Sodium "	1·70	85·05	50·03
Lithium "	1·60	69·00	42·86

These numbers show that the affinity-coefficients are directly proportional to the formula-weights of the nitrates, and that (with one exception) a and Σ increase and diminish in regular order. The quotients, Q, therefore represent the masses of nitrates which correspond with what Mill calls a 'unit of elective attraction.'

Chemical Systems of limited action.

When a chemical reaction is expressed symbolically either as AB + CD = AC + BD or A′ + B′ = C′, it is usually understood that for the complete decomposition of the mass AB all that is necessary is to bring it into suitable contact with the definite mass of the second body CD, or that the

nage A' if presented to B' under proper conditions will unite with it to form C'. In many chemical changes this is true, at least within the limits of experimental error, and if sufficient time be given; and it may be said that many processes of quantitative chemical analyses are based on this assumption. There are, however, many instances known in which the statement does not hold good. For example, if mol. weights of ethylic alcohol and acetic acid are mixed and heated for some time, say at 100°, only about 66 p.c. of the total action possible takes place, no matter how long the operation is allowed to continue; or again, if mol. weights of iodine and hydrogen are heated at 440° in a closed vessel, even after an indefinitely long period of time there will still exist a certain fraction of these elements uncombined. The limitation of these and many other similar changes appears to be due to the fact that the products of the first action tend, under the conditions of the experiment, to re-form the original substances, and the two reactions proceed simultaneously with different degrees of intensity, depending upon the masses of material, until a stage is reached at which a state of equilibrium is attained, the first action at this stage being balanced by the second. The mutual action of alcohol and acetic acid would thus be represented by the equations,

(1) $CH_3CO_2H + C_2H_5OH = CH_3CO_2C_2H_5 + H_2O$,
(2) $CH_3CO_2C_2H_5 + H_2O = CH_3CO_2H + C_2H_5OH$.

The theory of such limited actions was formulated by Guldberg and Waage, in 1867 (*Études sur les Affinités chimiques*) and applied by them to the determination of the 'coefficients of affinity' for several reactions. These chemists concluded from the results of their experiments that in a system undergoing change the amount of action in a unit of time between two or more active bodies—in other words, the rate of the change—is proportional to the product of the active masses. This same assumption was made by Berthelot in 1862, based on the results of his etherification experiments; and in 1866 Harcourt and Esson showed that for certain chemical systems the rate of change is proportional to the product of the active masses of the changing bodies. In the above statements the 'active masses' of the various bodies means the number of equivalents of each present in the reacting system. There are instances, however, in which bodies introduced into a chemical system either accelerate or retard the reaction without themselves undergoing change (*v. post*, p. 714). Guldberg and Waage assume that, in the reaction $A + B = A' + B'$, if the masses of A and B be p and q, then the force tending to produce the change varies as the product pq, whatever may be the kinds of matter; for two particular substances this force is equal to κpq, where κ is the 'coefficient of affinity' depending upon the kinds of matter, and probably upon the conditions of the experiment (*v. ante* and also AFFINITY, pp. 70–75). This, however, is not the only force acting; there are others of a secondary character tending to retard or accelerate the formation of A' and B'. Neglecting these secondary forces for the present, let the masses of A' and B' be p' and q', and the coefficient of affinity for the reverse action $A' + B' = A + B$ be κ', then the force tending to re-form A and B equals $\kappa' p'q'$. When equilibrium is attained these two forces are equal, or $\kappa pq = \kappa' p'q'$, so that if the four quantities p, q, p', q', are determined experimentally, the ratio $\frac{\kappa}{\kappa'}$ of the coefficients of affinity may be found.

Expressed in another way, if P, Q, P', Q', be the number of equivalents of the four substances in the system at the beginning of the reaction, and if x be the number of equivalents of P and Q transformed into P' and Q' when equilibrium is reached, or no further change takes place in the system, all expressed in terms of unit volume, then $p = P - x$, $q = Q - x$, $p' = P' + x$, and $q' = Q' + x$; inserting these values, the equation becomes $\kappa(P - x)(Q - x) = \kappa'(P' + x)(Q' + x)$.

Such is the simplest representation of the theory of limited actions. The presence, however, of extraneous salts, or even the secondary actions among the four bodies themselves, doubtless materially influence the ultimate limit when a state of equilibrium is reached. For instance, if a body X be introduced into the system, Guldberg and Waage assume that the force produced by the action between X and A, and influencing the change between A and B, is proportional to the product of X and A, or is equal to aAX, and they term a the 'coefficient of action.' Assuming that there are coefficients of action between all the four bodies—these coefficients being a, b, c, and d, for A and A', A and B, B and A', and B and B', respectively, and a', b', c', d', for A' and A, B and A, A' and B, and B' and B, respectively—then the total force for the reaction between A and B will be equal to

$$\kappa pq + app' + bpq' + cqp' + dqq',$$

and that between A' and B' will be equal to

$$\kappa' p'q' + a'p'p + b'pq' + c'p'q + d'q'q.$$

But that there may be equilibrium these forces must be equal. Writing $a - a' = \alpha$, $b - b' = \beta$, &c., the equation of equilibrium becomes

$$\kappa pq = \kappa' p'q' + \alpha pp' + \beta pq' + \gamma qp' + \delta qq'.$$

If it is desired to study the rate at which the reaction progresses, then this rate is assumed to be measured by the difference between the two forces or

$$\frac{dy}{dt} = \kappa pq - \kappa' p'q' - \alpha pp' - \beta qq' - \gamma p'q - dqq'.$$

Owing to their complicated character, these equations for the limit or the rate of a chemical change are of little value from an experimental point of view; it would seem scarcely possible to determine the numerous secondary forces Guldberg and Waage introduce into their formulæ. In such a case as the action between barium sulphate and potassium carbonate the secondary actions to be taken into account are between $BaSO_4$ and $BaCO_3$, $BaSO_4$ and K_2SO_4, K_2CO_3 and $BaCO_3$, K_2CO_3 and K_2SO_4, and between the water and each of the four salts. For a full discussion of this theory in its simpler form applied to experimental results see Guldberg and Waage, *J. pr.* [2] 19, 69 (*v.* also AFFINITY, p. 75).

Berthelot and Saint-Gilles (*A. Ch.* [3] 65 385; 66, 1; 68, 225) were the first to make a complete study of the reactions between carbon acids and alcohols, as regards the influence exerted by variations of temperature, pressure

amounts of material, and time. They found that these reactions are characterised by three important features: (1) the combination proceeds slowly, with a velocity depending upon the influences to which the system is submitted; (2) the combination is never complete, however long the duration of contact; (3) the proportion of ethereal salt formed under different conditions always tends towards a limit.

The inverse action limiting the formation of the ethereal salt, viz. its decomposition by the water formed during the reaction, was found to be much less rapid than the combination. In other words, if two systems are employed—one consisting of ethylic alcohol and acetic acid, the other of ethylic acetate and water—all in equivalent proportions, the first of these will attain the limit of equilibrium more quickly than the second under like conditions. Berthelot (*A. Ch.* [3] 66, 113) concluded that in the formation of the ethereal salts 'the quantities of acid and alcohol that combine at each instant are proportional to the product of the reacting masses.' He gave the formula for expressing the rate of formation as $\frac{dy}{dt}=m\nu\mu\left(1-\frac{y}{l}\right)^2$, for equivalent quantities of alcohol and acid, where l is the limit, which for acetic acid is = 66·5.

According to the theory of mass-action, the rates of formation of ethereal salts, as well as the magnitude of the limits, ought to be increased by an increase in either the amount of alcohol or of acid. As regards the ultimate limits, this was found to be true by Berthelot and Saint-Gilles, but for the speed of etherification they found that with n equivalents of alcohol and one of acid there was (at least for part of the course) little or no increase over that for equivalent quantities; in fact, a diminution in the rate was observed. On the other hand, with n equivalents of acid and one of alcohol the rate of etherification was greatly accelerated. The following two tables illustrate these points (*A. Ch.* [3] 66, 90, 98):—

1 eq. acetic acid + n eq. alcohol. Temp. 100°.

	$n=1$, acid = 100, limit = 100		$n=2$, acid = 100, limit = 100		$n=5$, acid = 100, limit = 100	
4 h.	25·8	38·8	27·8	33·8	17·5	19·3
15 ,,	47·4	71·3	44·0	53·2	31·3	34·5
83 ,,	60·6	91·1	72·2	87·1	72·2	79·4

1 eq. alcohol + n eq. acid. Temp. 100°.

	$n=1$, acid = 100, limit = 100		$n=2$, acid = 100, limit = 100		$n=5$, acid = 100, limit = 100	
4 h.	25·8	38·8	47·1	54·9	57·6	59·4
15 ,,	47·4	71·3	74·4	86·7	96·6	100
83 ,,	60·6	91·1	79·2	92·5	96·6	100

The variation produced in the limit, or maximum amount of ethereal salt formed, by employing excess of one or other of the constituents is illustrated by the following tables (*A. Ch.* [3] 68, 274, 286):—

1 eq. acid + n eqs. alcohol. n	limit
1·0	66·5 p.c.
1·5	77·9
2·0	82·8
2·8	85·6
3·0	88·2
4·0	90·2
5·4	92·0
12·0	93·2
19·0	95·0
500·0	neutral to litmus.

n eqs. acid + 1 eq. alcohol n	limit
1·0	66·5 p.c.
·67	51·9
·50	41·4
·36	30·6
·33	29·3
·25	22·6
·18	17·1
·08	7·8
·05	5·0

The action of inorganic acids on alcohols has been investigated by Villiers (*A. Ch.* [5] 21, 72); but in these processes secondary reactions that are liable to occur complicate matters somewhat. With a given alcohol, the speeds of etherification of the acids HI, HBr, HCl, and H_2SO_4, were found to be widely different. HI etherifies more quickly than HBr, and each more quickly than acetic acid; whereas HCl acts with extreme slowness, even much more slowly than acetic acid. H_2SO_4 etherifies almost immediately under ordinary conditions, but the speed is diminished by dilution, as well as by lowering the temperature. The etherification limits at 100° are different for the three hydracids, and are greater than the corresponding limits at lower temperatures. The limits also depend upon the proportion of water which exists in the initial mixture, but while the limit diminishes in the case of organic acids in a continuous manner as the water increases, without actually becoming *nil*, the etherification by hydracids ceases completely with a certain dilution, and this limit of dilution is not fixed but rises rapidly as the temperature rises. With H_2SO_4, the etherification is completely stopped with a certain proportion of water, but, contrary to what occurs with the hydracids, increasing the temperature to 100° does not cause the reaction to take place. From a consideration of the work of Berthelot and Saint-Gilles on the rate and conditions limiting the etherification of alcohols by organic acids, it would seem natural to conclude that the application of the methods employed by these chemists to the various cases of isomerism among alcohols and acids would yield important results relating to the structure of such bodies. For the purpose of discovering whether any relation exists between the rate and limit of etherification and the isomeric structure of either of the two active bodies taking part in the reaction, Menschutkin (*A. Ch.* [5] 20, 289; 23, 14; *J. pr.* [2] 24, 49; 25, 193) has made an elaborate study of the action of organic acids on alcohols. In order to render all the results comparable with each other it was necessary to assume two standards for reference, one for the alcohols and another for the acids. Methylic alcohol was chosen as the standard alcohol; and formic acid as the standard acid. The two characteristics chosen for measurement were (1) the initial speed of etherification, or the amount of action that takes place in the first hour, and (2) the final limit of the process; these Menschutkin terms the 'etherification-data.' For the 'methylic-acetic' system Menschutkin took the limit as equal to 100; that is to say, out of equal numbers of molecules of methylic

alcohol and acetic acid (in this case [illegible]4) only 100 molecules were converted into ethylic acetate when the system reached a state of equilibrium; of these 100 molecules, [illegible]0 were formed during the first hour of action.

The following table contains the 'etherification-data' for the primary alcohols employed:—

Alcohol	Speed	Limit
Methylic, HCH_2OH	80	100
Ethylic, CH_3CH_2OH	67·3	95·6
Propylic, $C_2H_5CH_2OH$	66·9	96
Butylic, $C_3H_7CH_2OH$	67·4	96·6
Octylic, $C_7H_{15}CH_2OH$	67·0	?

The influence of isomerism on etherification among the primary alcohols was investigated for the case of isobutylic alcohol; the data obtained were

Isobutylic, $C_3H^\beta{}_7CH_2OH$, speed = 64·6 limit = 96·6.

These numbers show that the limit is unaffected, but that there is a small decrease in the speed. The unsaturated primary alcohols showed less facility for forming ethers, the reaction in their case progressing much less rapidly, as the following numbers show:—

	speed	limit
Allylic alcohol, $C_2H_3CH_2OH$,	51·9	85·3
Propargylic alcohol, C_2HCH_2OH,	29·5	?
Benzylic alcohol, $C_6H_5CH_2OH$,	54·6	87·3

For the secondary alcohols, the phenols, and some other alcohols, the following etherification-data were obtained:—

		Speed	Limit
Dimethyl carbinol	$(CH_3)_2CHOH$	38·2	86·9
Methylethyl "	$(CH_3)(C_2H_5)CHOH$	32·5	85·2
Diethyl "	$(C_2H_5)_2CHOH$	24·3	84·2
Isopropylmethyl "	$(CH_3)(C_3H^\beta{}_7)CHOH$	27·2	85·2
Isobutylethyl "	$(C_2H_5)(C_4H^\beta{}_9)CHOH$	26·?	?
Hexylmethyl "	$(CH_3)(C_6H_{13})CHOH$	34·1	?
Ethylvinyl "	$(C_2H_5)(C_2H_3)CHOH$	2[illegible]·3	75·1
Diallyl "	$(C_3H_5)_2CHOH$	15·3	72
Ethylphenyl "	$(C_2H_5)(C_6H_5)CHOH$	27·2	?
Diphenyl "	$(C_6H_5)_2CHOH$	31·6	?
Phenol "	$C_6H_5.OH$	2·0	[illegible]·4
Paracresol "	$C_6H_4CH_3.OH$	3·7	13·7
Thymol "	$C_6H_3CH_3C_3H_7.OH$	1·4	13·6
α-Naphthol "	$C_{10}H_7.OH$	?	8·8
Glycol "	$CH_2OH.CH_2OH$	61·7	77·4
Glycerin "	$(CH_2OH)_2CHOH$	52·3	66·2
Erythrite "	$C_4H_6(OH)_4$	34	57·6
Mannite "	$C_6H_8(OH)_6$	29·6	38

Menschutkin (*J. pr.* 25, 193) has also determined the initial speeds and limits for different organic acids, employing one alcohol (isobutylic), and taking formic acid as the standard of reference. The following results were obtained:

	Acid	Speed	Limit
$C_nH_{2n}O_2$	Formic CH_2O_2	100	100
	Acetic $C_2H_4O_2$	71·9	104·8
	Propionic $C_3H_6O_2$	66·7	106·9
	Butyric $C_4H_8O_2$	65·9	108·2
	Caproic $C_6H_{12}O_2$	53·6	108·7
	Caprylic $C_8H_{16}O_2$	50·0	110·3
	Hydrosorbic $C_6H_{10}O_2$	69·7	100·4
	Phenylacetic $C_8H_8O_2$	79·1	115
	Phenylpropionic $C_9H_{10}O_2$	65·2	112·1
	Dimethacetic $CH(CH_3)_2CO_2H$	43·4	108·2
	Methethacetic $CH(CH_3)(C_2H_5)CO_2H$	30·3	114·8
	Crotonic $C_3H_5.CO_2H$	19·6	112·3
	Cinnamic $C_2H_2(C_6H_5)CO_2H$	18·7	116·3
	Trimethacetic $C_5H_{10}O_2$	11·8	113·1
	Dimethethacetic $C_6H_{12}O_2$	4·8	115·4
	Sorbic $C_6H_8O_2$	12·9	116·3
	Benzoic $C_7H_6O_2$	13·9	112·9
	Nitrobenzoic $C_7H_5(NO_2)O_2$	40·1	114·3
	Paratoluylic $C_8H_8O_2$	10·7	119·1
	Cuminic $C_{10}H_{12}O_2$	10·1	118·1

From the foregoing numbers it is seen that the rates of etherification of the secondary acids are much less than those of the primary acids, but that the limits show only slight variations. The speeds of etherification of the tertiary acids are less than those of either the primary or secondary acids, but on the other hand the limits are greater. For a full discussion of the value of etherification-data as a means of determining isomerism among alcohols and acids see Menschutkin (*J. pr.* [2] 26, 103; also *Z. P. C.* 1, 611).

The theory of limited chemical reactions has been formulated in a simple manner by Van 't Hoff (*B.* 10, 669) for the particular case of etherification, but essentially in the same manner as Guldberg and Waage have done in their general treatment of this chemical problem. If the system initially consists of one equivalent of acetic acid, κ of alcohol, and q of water, then when the quantity ϵ of ether has been formed, there will still remain of acid $1-\epsilon$, of alcohol $\kappa-\epsilon$, and of water $q+\epsilon$; consequently the rate at which ether is still being formed is expressed by $C_1(1-\epsilon)(\kappa-\epsilon)$, and the rate of decomposition of the already formed ether by the water by $C_2\epsilon\ (q+\epsilon)$. When equilibrium is attained these two expressions must be equal, or, $C_1(1-\epsilon)(\kappa-\epsilon) = C_2\epsilon(q+\epsilon)$. For equivalent quantities of acetic acid and ethylic alcohol, or $\kappa=1$ and $q=0$, Berthelot and St. Gilles found the limit to be about 66·6 p.c., or $\epsilon = \dfrac{2}{3}$. Inserting these values in the equation, the ratio of the two constant C_1 and C_2 is found; or $C_1 = 4C_2$. The equation now becomes $4(1-\epsilon)(\kappa-\epsilon) = \epsilon(q+\epsilon)$ from which the maximum quantity of ether capable of being formed when various amounts of alcohol or water are employed can be calculated. For instance, if $\kappa=\infty$, *i.e.* if the alcohol is unlimited in amount, $\epsilon=1$, that is, all the acid is changed into ethereal salt; if $q=\infty$, *i.e.* if the water is unlimited in amount, $\epsilon=0$, or no ether is formed. These results are merely the extreme cases of what experiments have proved to be true between those limits of κ and q which have been tried.

Formation of Acetanilide.—In a study of the formation of acetanilide, according to the equation $C_6H_5NH_2 + C_2H_4O_2 = C_6H_5(C_2H_3O)HN + H_2O$, Menschutkin (*J. pr.* 26, 208) found that, although in the processes of etherification the final limit of the reaction attained after an indefinitely long interval of time is practically uninfluenced by change of temperature, in this example the limit is materially decreased as the temperature increases. The following results show this decrease:—

Temp.	Limit.
100°	85·05 p.c.
125°	83·11
135°	82·39
145°	81·2[illegible]
155°	79·6[illegible]

Another remarkable fact was noticed in this

reaction, and one which is apparently at variance with most experiments relating to the action of mass (see Berthelot's etherification experiments, *ante*). In any chemical system undergoing change, comprising two or more active bodies, the rate of change is generally accelerated (*v.* p. 741) by an increase in the amount of any of the active bodies, and this increase in the rate is more or less proportional to the quantity of active substance added. But in the formation of acetanilide, with a constant amount of acetic acid, an increase in the quantity of aniline retards the action, according to Menschutkin, although the final limit is increased as the theory of mass-action requires. The numbers under 'speed' showing this fact represent the amount of action after 15 mins.

Molecules aniline with one mol. acid	Speed	Limit
1	34·71	79·68
2	28·71	91·65
3	23·45	94·61
4	—	96·17
8	17·13	97·22

However, when the aniline remains constant and the acetic acid is increased, the law of mass-action appears in the normal way (*v.* also AFFINITY, p. 85).

Molecules acid with one mol. aniline	Speed	Limit
1	34·71	79·68
2	57·30	96·88
4	78·08	99·80

Division of a base between two acids.

When a mixture of two acids acts on a base, or two bases act on one acid, the two acids in the first case being more than sufficient to combine with the base, or the two bases in the second case with the single acid, it is usually granted that the base divides itself between the two acids or the acid between the two bases in definite ratios. Or if an acid acts upon a salt in solution, as nitric acid on potassic sulphate, a definite amount of change takes place resulting in this instance in the formation of potassic nitrate and sulphuric acid. If the ratios in which such divisions occur were known they might afford measures of the relative affinities of the acting bodies for the particular conditions of the experiments. Such ratios have been determined for a great many acids by Ostwald, with most important results. (For an account of this work *v.* AFFINITY.)

Pattison Muir (*C. J.* 33, 27; 35, 311; 36, 60) has studied the conditions affecting the equilibrium of certain chemical systems wherein pps. are formed, with the view of determining the relationship between the concentrations of the solutions, the ratios between the active bodies, and the influence of heat on the equilibrium ratios. An investigation somewhat similar to this was conducted by Morris (*A.* 213, 233).

Fractional Precipitation.

It has been shown (*ante*; and *v.* AFFINITY) that if a mixture of two acids is allowed to act upon a single base, or of two bases on a single acid, the ratio in which the base divides itself between the two acids, or the acid between the two bases, depends upon the relative quantities or masses of the materials in the system, as well as upon the strength of the affinities acting between the several bodies. In like manner, if a pptant. is added to a solution, containing two or more salts of different metals, the mass of the pptant. being less than is required for complete ppn. of all the salts in the solution (being, say, $\frac{1}{\mu}$th of the total necessary) then the ratios of the quantities of the salts decomposed—or of the hydrates, carbonates, &c. formed—depends on (i) the relative masses of the substances in solution, (ii) the relative affinities of the salts or the basic powers of the oxides with reference to the pptant., and also (iii) on the fraction of the total material that is ppd.

This highly interesting subject of fractional ppn. has been as yet investigated but to a very slight extent; it would, however, seem to promise in the future a fertile field for the determination of what might be called the relative basic powers of different oxides or hydrates. If, for example, a solution contains two salts of different metals, the basic powers of whose oxides are different, and if a small fraction is ppd. (say as hydrate), there will be a tendency on the part of the less basic material to accumulate in the pp. in preference to the more basic, and this tendency will be greater as the difference between the basic powers is greater. If the basic powers differ but slightly, then the increase in the ratio of the less to the more basic material will progress very slowly by repeated application of the process of fractional ppn. If in the extreme case no such difference exists under the conditions of the experiment as regards temperature and quality of the pptant. (the ratio of the basic powers may and probably does vary with the temperature), then the ratio of the two materials in the small pp. will be the same as that in the original solution, and consequently, however frequently the process may be repeated on each fraction formed, no separation will be effected.

At the present time there are a number of elements known belonging to the earths, for the separation of which the only method that has yet been discovered is that of fractional ppn., or fractional fusion; in both cases the separation depends on the differences of the basic powers of the various bodies. Such, for instance, is the separation of the three elements, samarium, didymium, and lanthanum, from each other; or holmium, thulium, and erbium; or again terbium from yttrium. These separations are so extremely tedious, requiring the application of fractional ppn. to be repeated a very great number of times with but relatively infinitesimal yields of finally pure material, that it is evident that the differences in basic powers must be extremely small, more particularly in the cases of samaria-didymia, yttria-terbia, and holmia-thulia. This process for effecting the separation of these earths is rendered all the more uncertain and difficult owing to the want of facts drawn from the study of fractional ppn. of other bodies bearing upon

the best conditions under which the process should be conducted (v. EARTHS).

Chiżyński (*A. Suppl.* 4, 226; *J.* 1866. 12) has investigated the subject of fractional ppn. for the case of magnesium and calcium chlorides by phosphoric acid. This chemist employed solutions containing the two salts in varied proportions; to these solutions he added a constant quantity of phosphoric acid insufficient for complete ppn., then ammonia was added, and he determined the amounts of calcic and magnesic oxides in the pps. The composition of the pps. was found to vary with the ratio of the amounts of calcic and magnesic chlorides in the solutions, but to be nearly independent of the quantity of water used for dilution. By increasing the amount of calcic chloride in the solution, the magnesic chloride remaining constant, it was found that the lime passed into the pp. in greater quantity, while the amount of magnesia decreased; with the calcium salt constant, the magnesic chloride being increased, the reverse occurred, but to a less marked degree. These variations took place in a regular manner as the composition of the solutions varied.

Mills, in conjunction with others (*P. M.* [5] 13, 169, 177; and *Pr.* 29, 181), has studied the fractional ppn., by means of sodium hydrate or carbonate, of several sulphates, taken in pairs under varying conditions of mass, with the view of determining the relative facility with which one sulphate is decomposed in presence of another when an insufficiency of a pptant. is added to the solution.

In one set of experiments in which nickel and manganese sulphates were employed, the following numbers were obtained; each solution contained 1 gram of material made up to 100 c.c., and 10 c.c. of a solution of Na_2CO_3 (·5715 gram Na_2CO_3) were added:—

$NiSO_4$	$MnSO_4$	$NiSO_4$ ppd.	$MnSO_4$ ppd.	Temp. C.°
·1 grm.	·9 grm.	·0953	·5850	12·9
·2	·8	·1852	·4616	13·6
·3	·7	·2799	·3766	12·5
·4	·6	·3588	·2976	13
·5	·5	·4305	·2450	13·6
·6	·4	·4788	·1536	12·8
·7	·3	·4991	·1089	17
·8	·2	·5584	·0722	17
·9	·1	·5841	·0363	15·2

From these numbers it is seen that the ratio of the quantities of material ppd. varies continuously, and in the same manner as the ratio of the amounts of salts employed; with equal masses of the two sulphates in solution the pp. contains much more nickel than manganese; hence it is at once inferred that the basic power of manganous hydrate or oxide is greater than that of nickel, since the less basic a material the greater its tendency to be affected by the pptant.

Extending these experiments performed in a similar manner to mixtures of nickel and cobalt sulphates, but employing sodic hydrate instead of carbonate, it was found that these two salts have almost equal degrees of precipitability; that is to say, if the two salts exist in the solution in equal amounts they will accumulate in the pp. in about equal quantities; or, with varying quantities of material, the ratio of the amounts of the two salts ppd. will be approximately equal to the ratio initially in the solution; in other words, the basic powers of the two salts are about equal. (For the theory of fractional ppn. see Hood, *P. M.* 1886.)

Reduction of Oxides.

The conditions that affect the reduction of metallic oxides by hydrogen, carbon monoxide, and carbon, have been examined by Wright and Luff (*C. J.* 33, 1, 509; 35, 475; 37, 757), the type of the reactions being represented by the equation A + BC = AB + C. The results have important practical bearings on metallurgical operations. The temperature at which reduction commences is a function of (1) the physical conditions of the bodies experimented with, (2) and the chemical nature of the substances. With CO as the reducing agent, the temperature at which action begins in the case of cupric oxide varies from 60° to 146° according to the state of aggregation of the copper oxide; for ferric oxide the temperature ranges between 90° and 220°. The reduction by CO of copper oxide, prepared by ppn., is well marked at temperatures below 100°, but at 100° it becomes very energetic. The initial action of H on copper oxide was found to take place at temperatures ranging between 85° and 172°, and on ferric oxide between 195° and 265°. When carbon was employed as the reducing agent, the temperature of initial action varied not only with the physical nature of the metallic oxide, but also with the quality of the carbon; the temperature limits for copper oxide were 350° and 440°, and for ferric oxide 430° to 450°. By comparing the temperatures of initial action for a given kind of metallic oxide, it was invariably found that that reducing agent begins to act at the lowest temperature which has the greatest heat of combustion, so that the heat disturbance during its action has (algebraically) the greatest value. Thus H always begins to act at a lower temperature than carbon, and CO at a lower temperature than H, as the following table shows for different specimens of metallic oxides:—

	CO	H	Sugar C	C from CO
Cupric oxide A	60°	85°	390°	350°
" B	125	175	430	350
" C	146	172	440	430
Cuprous oxide	110	155	390	345
Ferric oxide A	202	260	450	430
" B	90	195	450	—
" C	220	245	450	430

Comparing cupric and ferric oxides prepared by analogous processes, and therefore presumably in much the same physical state, it was uniformly found that the temperature of initial action of a given reducing agent is lower on oxide of copper than on oxide of iron, as the following numbers show:—

		CO	H	Sugar C	C from CO
Oxides prepared by precipitation .	Copper	60°	85°	390°	350°
	Iron	90	195	450	430
Oxides prepared by heating salts . .	Copper	125	175	430	390
	Iron	202	260	450	430
		220	245	450	430

The extension of these experiments to the oxides of nickel, cobalt, lead, manganese, ferrous and ferroso-ferric oxides, resulted in the following conclusions, among others. Differences in physical state are attended with correlative differences in the temperatures at which the actions of the reducing agents CO, H, and C, are first manifested. For the several oxides of the same metal the temperature of the initial action of a given reducing agent is sensibly the same unless the differences in physical structure are very marked. In no case was any exception found to the rule that the temperature of initial action of CO is lower than that of H, and that of H lower than that of C, on the same sample of metallic oxide. For a large number of cases the rule holds that the greater (algebraically) the heat production during the occurrence of a reaction the lower is the temperature at which this action is first manifested.

During the investigation of the rates of action of CO and H, it was noticed that in many instances 'chemical induction' manifested itself; *i.e.* the reducing action of the gas on the metallic oxide at a given temperature was at first slight or nil ('period of incubation'), but after a longer or shorter time the reduction commenced and proceeded at an increasing rate, until the retarding influences of the products of the action caused the rate of reduction to cease increasing, and subsequently to diminish. The 'period of incubation,' when measurable, was found to be shorter the higher the temperature.

A similar phenomenon has been observed by Bunsen and Roscoe in their investigation of the action of light on a mixture of chlorine and hydrogen (*v.* INFLUENCE OF LIGHT, *post*), and it is interesting to note that in a heterogeneous system consisting of a solid oxide and a gas chemical induction should also manifest itself. The question naturally arises whether or not it is a general phenomenon accompanying all chemical changes.

Homogeneous Unlimited Systems.—Considering the simplest chemical system undergoing change, that of a single body either decomposing, like ammonium nitrate when heated, or suffering molecular rearrangement, as ammonic cyanate into urea, it is evident that unless the products interfere as retarding agents the amount of change in unit of time, that is to say the rate of change, will be proportional at any time to the amount of active substance then existing. When, however, a system comprises two or more active members reacting on each other, such as an alcohol on an acid, or hydric peroxide on an acidulated solution of a soluble iodide, the circumstances are much more complicated. The general experiments on the rate of chemical change, when not limited by inverse action, prove that in such complex systems the rate of change of any one of the members is increased or diminished by an increase or decrease in the quantity of any of the other constituents, and is more or less proportional to such variation. For example, if the system comprises $A_1A_2A_3 \dots A_n$ (different bodies reacting one with the other), the rate at which A_κ changes is increased or diminished by a similar variation in any other member, as A_r. The statement of this law of mass by Mills (*P. M.* [5] 1) in the words 'no matter what may be the masses of the substances reacting the entire mass of each takes part in the process,' requires to be limited by the further statement that the law applies only to homogeneous systems in the sense in which these have been before defined. It could not be asserted for instance that the entire mass of the marble in Bojuski and Kajander's experiments affects the rate of action of the acid, or that a hollow sphere of zinc dissolves less rapidly in acid than a solid sphere of similar external dimensions.

Berthelot in 1862 (*A. Ch.*) showed that the rate of reaction of alcohol with acetic acid is proportional to the product of the two active substances. Harcourt and Esson in 1866 (*Pr.* 14, 470) established several formulæ representing various experimental conditions based on the same hypothesis, but the reaction they employed for verification of the theory (permanganate on oxalic acid) proved to be of so complex a character as to give but imperfect results. These chemists, however, were more successful subsequently (*Pr.* 15, 262) with the reaction

$$H_2O_2 + 2HI = 2H_2O + I_2.$$

The theory of Guldberg and Waage relates more particularly to cases of limited action, but in its application to the study of the rate of change the introduction of so many 'coefficients of action' (*v. ante*, p. 737) renders the equation of little practical use for such investigations (But *v.* article AFFINITY, p. 70). Except in the theory of Guldberg and Waage, the influence of the products of the change either as accelerating or retarding agents is generally overlooked in attempts to formulate chemical action; but it is easy to introduce these effects in an equation to represent the rate of change of a complex system on the hypothesis that the rate is directly proportional to the product of all the active members and is inversely proportional to the amount of chemically inactive bodies formed (*v.* RETARDATION OF CHEMICAL CHANGE, p. 744).

In a complex system, consisting of n members undergoing change, let the masses of the initial active bodies be represented by $A_1A_2A_3 \dots A_n$, and let the masses of these bodies that have become changed or rendered chemically inactive up to time t, be represented by $\alpha_1, \alpha_2, \alpha_3 \dots \alpha_n$; then, according to this hypothesis, the rate of change of any member of the system, say A_κ, is

$$\frac{d\alpha_\kappa}{dt} = \mu \frac{(A_1 - \alpha_1)(A_2 - \alpha_2) \dots A_n - \alpha_n}{B \pm (\lambda'\alpha_1 + \lambda''\alpha_2 \dots \lambda^n\alpha_n)} \quad \dots \quad (1)$$

Where μ, and B, are constants, and λ', λ''...... are the retardation or accelerating coefficien[ts] of the products of the action, the + or − si[gn] being taken according as these products all a[ct] as retarding or as accelerating agents. Whi[ch] of these actions was performed by any specifi[c]

product of the primary action could be determined experimentally, by introducing a known mass of the body into the system, and comparing the rate of the change with that observed when no more of the specified body was present than was formed during the primary reaction. Since A_κ is the member of the system whose rate of change is the object of measurement, let the amount that remains unchanged at time t, that is $A_\kappa - a_\kappa$, be taken as y; then—if the initial quantities of the other members be $\nu_1, \nu_2, \ldots \ldots \nu_n$ equivalents of $A_\kappa, -A_1 = \epsilon_1\nu_1 A_\kappa$, $A_2 = \epsilon_2\nu_2 A_\kappa, \ldots \ldots A_n = \epsilon_n\nu_n A_\kappa$, and $a_1 = \epsilon_1 a_\kappa$, $a_2 = \epsilon_2 a_\kappa, \ldots \ldots a_n = \epsilon_n a_\kappa$. Inserting these values in the above equation it becomes

$$-\frac{dy}{dt} = \mu' \frac{y\{(\nu_1 - 1)A + y\}\{(\nu_2 - 1)A + y\}\ldots\text{etc.}}{B' \mp y} \quad (2)$$

In this equation μ' and B' are constants to be determined experimentally, A being the initial value of y; μ' is proportional to the rate and is dependent on the temperature (*v.* INFLUENCE OF HEAT ON CHEMICAL CHANGE, p. 744).

Numerical examples of this equation for a system comprising the three bodies, ferrous chloride, hydric chloride, and potassic chlorate, have been given by Hood (*P. M.* [5] 20, 444), but the solutions he employed were so dilute that the products of the action appeared to influence the rate inappreciably, consequently the term in the equation relating to these effects was neglected, and the equation was taken as:

$$-\frac{dy}{dt} = \mu' y\Big(\nu_1 - 1)A + y\Big)\Big((\nu_2 - 1)A + y\Big) \quad . (3)$$

for the system of three bodies.

It is possible to arrange the experimental conditions in such a way that, neglecting the action of the products, the course of the change may be much simpler than is represented by equation (2). This may be done, (1) by having all the active substances present in very large excess over that one which is made the object of measurement, so that they undergo but slight diminution between the beginning and the finish of the change taking place in the body measured; or (2) by arranging the constituents so that one or more of them, although taking part in the reaction, remains constant in amount, one constituent only diminishing in value. The equation for the rate of change of one member in either case would be by (2)

$$\frac{dy}{dt} = -\mu y A_1 A_2 \ldots A_n.$$

Where $A_1, A_2, \ldots A_n$ are the masses of the chemically active constituents which remain constant or nearly so; or integrating, $y = Be^{-at}$, a being equal to $\mu A_1, A_2 \ldots A_n$.

Harcourt and Esson (*T.* 157, 117) proved the truth of this exponential formula for the action between a soluble iodide and hydric peroxide. The fundamental change in this case is represented by $H_2O_2 + 2HI = 2H_2O + I_2$. By the simple device of adding a known constant amount of sodic thiosulphate to the active solution each time the liberated iodine made its appearance, the amount of hydric iodide was kept constant, while the H_2O_2 alone diminished. The successive additions of thiosulphate measured the amount of change of the hydric peroxide (or y), and the intervals between each addition, or rather the appearances of free iodine, measured the times of action. From their experiments relating to the influence of variations of temperature, and variations of the masses of the acting substances, Harcourt and Esson concluded that 'whether the solution contains in 1 c.c. 746 millionths of a gram of hydric sulphate or 150 times that quantity, 604 millionths of a gram of KI or 9 times that quantity, or whether HCl or hydric sodic carbonate be substituted for H_2SO_4, whether the temperature be 0° or 50°, and whether the portions of change require for their accomplishment intervals of one or two minutes, or intervals of half an hour or an hour, this reaction still conforms to the law that the amount of change is at any moment proportional to the amount of changing substance.'

Harcourt and Esson (*T.* 156, 193) had previously employed the reaction between potassic permanganate and oxalic acid for investigating the laws according to which a chemical change progresses. Although this investigation was not quite successful in its primary object, it serves well to illustrate the anomalous results that may be obtained by the interfering action of the products formed in a reaction, or by extraneous salts. The reaction under examination may be represented at its beginning and its conclusion by the two sides of the equation:

$$K_2Mn_2O_8 + 3H_2SO_4 + 5H_2C_2O_4$$
$$= K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

The reaction progresses with moderate rapidity at temperatures easily kept under control. By varying the mass of any one of the constituents a corresponding variation occurs in the rate of oxidation. The influence of H_2SO_4 is shown in the following table; the reaction was allowed to go on in each case for four minutes, and was then suddenly stopped by the addition of KI, the amount of change that had taken place being obtained by estimating the iodine liberated:—

Molecules H_2SO_4	Per cent. change in 4 min.	Molecules H_2SO_4	Per cent. change in 4 min.
2	21·8	10	71·6
4	36	12	77·4
6	51·1	14	82·2
8	63·5	16	85·7
		22	92·3

The principal secondary reaction in the oxidation of $C_2H_2O_4$ by $K_2Mn_2O_8$ arises from the decomposition of $K_2Mn_2O_8$ by the $MnSO_4$

$$(K_2Mn_2O_8 + 3MnSO_4 + 2H_2O$$
$$= K_2SO_4 + 2H_2SO_4 + 5MnO_2);$$

this reaction influences the rate of oxidation in a remarkable manner. With the materials in the proportions of $K_2Mn_2O_8$:$16H_2SO_4$:$5H_2C_2O_4$, it was found that when no manganous sulphate was added only eight p.c. of chemical change took place in 4 mins., but by gradually increasing the mass of $MnSO_4$ the amount of change taking place in this interval of time increased, until it reached 85 p.c. when $3MnSO_4$ was present. Further increase of the $MnSO_4$ only slightly altered the rate of oxidation. Harcourt and Esson likewise found that by varying the masses of H_2SO_4 and $C_2H_2O_4$, the $K_2Mn_2O_8$ and $MnSO_4$ remaining constant, the percentage of chemical change in a definite time (3 mins.) gradually increased till it reached

a maximum, then diminished to a minimum, and again increased on addition of more $H_2C_2O_4$. Experiments on the relation between the time of continuance of the action and its amount showed that after a certain interval the course of the change was represented by an hyperbola. The reason of this regularity only occurring after the action had proceeded some time was traced to the double changes that take place, first between the $MnSO_4$ and $K_2Mn_2O_8$, and then between the MnO_2 produced and the $C_2H_2O_4$. Both changes are, however, comparatively slow; but if either of them occurred very rapidly compared with the other, in presence of equivalent quantities of materials, the whole course of the change would doubtless be represented by an hyperbola.

Hood (*P. M.* [5] 6, 371; 8, 121) has studied the rate of oxidation of ferrous sulphate by potassic chlorate, and the influence exerted on the process by variations (i) in the amounts of acid used and (ii) in the temperature. The equation for equivalents being

$6FeSO_4 + KClO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + KCl + 3H_2O$, it is evident that the rate of change will be the product of three factors. The acid being in large excess and $KClO_3:6FeSO_4 = \nu:1$, the rate of change by equation (3) is $\frac{dy}{at} = -\mu B y(\nu-1)A + y$ where B equals the amount of acid; or $\log_e \frac{y}{(n-1)A+y} = \mu B(n-1)A(c-t)$; if, however, $KClO_3:6FeSO_4 = 1:1$, then $\frac{dy}{dt} = -\mu B y^2$, or $y(a+t) = \frac{1}{\mu B}$. By a series of determinations of y (c.c. of permanganate) at indefinite intervals of time, the constants in either of these equations (μB and c, and μB and a) were found for different conditions of temperature, amount of acid (B), &c., and consequently a measure was obtained of the changes produced in the rate of oxidation by such variations. Hood found that for this reaction both these formulæ hold good, and, as theory indicates, the rate of oxidation, within certain limits, is proportional to the amount of free acid; as the amount of acid, however, becomes comparatively very great the oxidation progresses much more rapidly than the acid increases. When HCl replaces H_2SO_4, in order to produce the same rate of oxidation the amounts must be as 36·5 : 80.

Ostwald (*J. pr.* 27, 1) has studied the interesting reaction $R.CONH_2 + H_2O = R.CO.ONH_4$ with reference to the accelerating influence acids have upon the rate of the change. This reaction is a striking instance of so called 'predisposing' affinity, the reaction being a very slow one when water alone is employed. (For details of this investigation, *v.* the article AFFINITY, p. 79.)

The decomposition of the ethereal salts, *e.g.* methylic acetate, by water, affords an example of chemical change somewhat analogous to that of the acetamides. The difference between the two cases is that in the former the water resolves the compound into two ethers, alcohol and acid, whereas in the latter the water is assimilated to form a more complex compound. The presence of acids greatly accelerates the decomposition of the ethereal salts, as is the case with the acetamides; the relations between speed of action and quality of acid have been investigated by Ostwald (*J. pr.* 28, 449), *v.* AFFINITY.

RETARDATION AND ACCELERATION OF CHEMICAL CHANGES.—In the reaction that takes place when an alcohol and an organic acid are mixed, the amount of change is limited by the inverse action that arises between the products of the change, ethereal salt and water, which inverse action tends to the re-formation of the original alcohol and acid; it is consequently evident that the rate at which the etherification progresses is retarded by this inverse action. In like manner if $BaSO_4$ is acted on by K_2CO_3, the rate of the decomposition is retarded by the inverse action that occurs between the $BaCO_3$ and K_2SO_4 which results in the formation of the original bodies.

The same may be said as regards the rate of all those reactions which are limited in extent by inverse chemical changes.

There is, however, another kind of retardation possible, not arising from any secondary chemical changes taking place in the system, but of a purely physical origin. If in a homogeneous system undergoing change, such for instance as is represented by the equation $A + B = AB$, the chemically active bodies be considered to be in a state of continual motion, the rate of formation of AB will be proportional to the number of impacts between the A's and B's in a unit of time. It is conceivable then that if the molecules AB are not removed from the sphere of action their mere presence will hamper the movements of the remaining A's and B's, and by so doing will diminish the number of impacts between them in a unit of time, that is to say, will retard their rate of combination. That retardation of a chemical change does arise by the addition of a quantity of one of the products has been shown to be true in several instances; but whether the effects are to be interpreted on a physical basis, as is done here, or on a chemical basis, cannot be decided with certainty until much more experimental evidence has been obtained. The study of the influence of chemically inactive bodies on systems undergoing change, that is to say of bodies which probably do not take part chemically in the reactions, forms a wide field for research; and there is no doubt that the results obtained will have an important bearing on chemical science considered in its dynamical aspect.

An acceleration in the rate of a chemical change may be brought about by an increase in the amount of any one of the active constituents of the system; such an acceleration, as has been already shown, is easily explained by the law of mass-action, viz. that the total mass of each constituent takes part in the reaction.

There are instances, however, somewhat more difficult of explanation, such as the inversion of cane sugar, or the decomposition of methylic acetate, by acids, wherein the addition of an acid merely accelerates the change, the mass of the acid remaining the same at the finish as at the beginning of the reaction. The tendency to undergo change in these instances is merely increased by the presence of the acid, and this tendency, measured by the speed of the change, is dependent on the character of the acid employed (*v.* Ostwald's experiments detailed in AFFINITY, p. 79). The difficulties that are here

encountered would seem to be similar to those that arise in the consideration of so-called 'contact actions' or catalysis.

Guldberg and Waage (*Études*), in their investigation of the rate of production of hydrogen by the mutual action of metals and acids, found that the presence of salts in the acid solution exercised a remarkable influence on the speed, some salts accelerating, others retarding, the reaction; the salts themselves remaining unaltered. Mills and Walton (*Pr.* 28, 268) observed an acceleration in the rate of formation of ammonia from potassic nitrate and zinc amalgam by the addition of either K_2SO_4 or Na_2SO_4, the increase of speed being practically the same for equal masses of the two sulphates. If a dilute acidulated solution of ferrous sulphate is oxidised by potassic chlorate at the ordinary temperature, these two bodies being present in equivalent quantities, and the free acid (H_2SO_4) being much in excess, the rate of the oxidation (*v. ante*) is expressed by the equation $\frac{dy}{dt} = -\frac{y^2}{b}$, or $y(a+t) = b$, where t is time in minutes, and y is c.c. permanganate equivalent to ferrous iron remaining at time t. Since in these equations $\frac{dy}{dt} \propto b^{-1}$ (or the rate of change is inversely proportional to b), by performing two experiments under like conditions of temperature, dilution, amount of acid, of iron, and of chlorate, except that to one of the solutions a known mass of a sulphate is added, it is easy to calculate the equations, $y(a+t) = b$, for each of the systems; and, by comparing the two values for b, to get a measure of the retarding action of the particular sulphate employed. In other words, the time required to oxidise the iron from y' to y'' is proportional to b, and if this time for the blank experiment be taken as 100 minutes, the value of $\frac{100b'}{b}$ (where b corresponds to the blank and b' to the retarded experiment) gives the number of minutes required to perform the same amount of oxidation in the presence of the added sulphate. The annexed table contains the results obtained by Hood (*P. M.* [5] 13, 419) in studying the retardation of various sulphates in the above manner; the temperature being 2½°C. in each experiment.

Weight of salt	K_2SO_4 $\frac{100b'}{b}$	K_2SO_4 Per cent. retardation for 1 gram	Na_2SO_4 $\frac{100b'}{b}$	Na_2SO_4 Per cent. retardation for 1 gram	$(NH_4)_2SO_4$ $\frac{100b'}{b}$	$(NH_4)_2SO_4$ Per cent. retardation for 1 gram
2 grams	120·3	10·1	120·6	10·3	120·8	10·4
3 "	130·8	10·2	131·[illegible]	10·5	132·4	10·8
4 "	143·1	10·8	143·3	10·8	145·[illegible]	11·3
5 "	153·4	10·7	151·9	10·4	154·9	10·9
6 "	167·1	11·2	166·5	11·1	166·[illegible]	11·0
8 "	195·8	11·9	190·5	11·3	193·2	11·6
10 "	221·7	12·2	212·4	11·2	213·9	11·4

Weight of salt	$KAl(SO_4)_2$ $\frac{100b'}{b}$	$KAl(SO_4)_2$ Per cent. retardation for 1 gram	$(NH_4)Al(SO_4)_2$ $\frac{100b'}{b}$	$(NH_4)Al(SO_4)_2$ Per cent. retardation for 1 gram
2 grams	112·2	6·1	111·8	5·9
3 "	118·1	6·0	118·3	6·1
4 "	124·7	6·2	124·4	6·1
5 "	129·6	5·9	129·7	5·9
6 "	138·1	6·3	137·4	6·2
8 "	146·2	5·8	141·5	5·6
10 "	155·2	5·5	153·1	5·3

Weight of salt	$MgSO_4$ $\frac{100b'}{b}$	$MgSO_4$ Per cent. retardation for 1 gram	$ZnSO_4$ $\frac{100b'}{b}$	$ZnSO_4$ Per cent. retardation for 1 gram
2 grams	114·9	7·4	110·1	5·0
3 "	123·6	7·8	115	5·0
4 "	128·4	7·1	117·5	4·4
5 "	134	6·8	123	4·6
6 "	140·9	6·8	127	4·5
8 "	150·9	6·4	132·7	4·1
10 "	161·1	6·1	138·4	3·3

The numbers show that the retardation occasioned by the presence of a chemically inactive salt in the system employed is proportional to the mass of the salt added, and that some salts of analogous character produce for equal masses the same retarding effect. Thus the potassium, sodium, and ammonium sulphates each produce a retardation of about 10 p.c. per gram, and the two alums about 6 p.c. per gram. The differences in the effects of magnesium and zinc sulphates are, however, too great to allow of their being classed together as analogous salts from a dynamical point of view with reference to this particular case of retardation.

Considering the alkali-sulphates and the alums, it is clear that, since equal masses of the several members of each group produce the same effect, the retardation produced by a molecule of one of the salts is proportional to its mass; in other words, the greater the mass of a molecule the more it retards the rate of the chemical change.

Judging by these facts, it would seem not improbable that chemical bodies might be classified on a dynamical basis as regards their retardation-effects. With this aim, Hood (*P. M.* [5] 20, 444) has continued these experiments in relation to soluble chlorides, but the anomalous results obtained do not justify the assumption started with. The results show that the sulphates of the alkali metals in the oxidation of ferrous chloride by $KClO_3$ produce an equal retarding effect, about 17 p.c. per gram, but that $MgSO_4$, $ZnSO_4$, and $CdSO_4$ (although usually classed together from a statical point of view) differ greatly in their retardation-effects; the results for the first two sulphates are in about the same ratio as in previous experiments with ferrous sulphate instead of ferrous chloride. Experiments with $MgSO_4$ showed that these 'retardation coefficients' vary slightly with increase of temperature.

An examination of the effects of chlorides on this reaction showed strikingly anomalous results; no two chlorides gave the same retardation-effect. Sodic chloride practically produced no effect on the speed of the oxidation, while zinc, magnesium, and cadmium chlorides produced an acceleration. It seems difficult to reconcile these results with a theory that should account for the action of a chemically inactive

alt in a system undergoing change on the basis f molecular interference with the movements f the changing constituents of the system. It nay be, however, that the presence of such xtraneous bodies induces secondary reactions n the system which occasion either an accelera-ion or a retardation of the principal change.

Influence of Heat.—The study of the in-uence exerted by heat on chemical changes, as llustrated by the phenomena of dissociation, nd by such phenomena as occur when phos-horus or sulphur are heated, forms an im-ortant factor in the vast problem of chemical ction. Starting with the fundamental notions, hat heat is a form of energy, and that all xternal material phenomena comprise two actors, matter and motion, which it is the aim f chemistry to investigate, with the molecular heory of the constitution of matter for a basis, t is evident that the relations between the ction of heat and chemical change will be most dvantageously studied by examining in what way he rates and the limits of chemical changes, occurring in homogeneous systems, are affected by heat, and by determining the influence exerted on such changes by extraneous bodies.

What is already known regarding the in-fluence of heat in bringing about chemical com-binations and decompositions would seem to indicate that such action is of a twofold cha-racter, more particularly in systems possessing free mobility either in the gaseous or liquid states; for, besides accelerating the motions of translation of the molecules of the system, and so multiplying the chances of collision in a given time, and consequently increasing the rate at which the change takes place, the action of heat also accelerates the rate of change by diminishing the stabilities of the reacting mole-cules, and thus increasing their tendency to undergo change. Thus, representing the mole-cules of gaseous iodine and hydrogen respectively as I_2 and H_2, the amount of HI produced in unit time at a given temperature, by the mutual action of H_2 and I_2, will depend upon the num-ber of molecular collisions, the velocities of translation of the molecules (or the temperature of the gas), as well as upon the facility with which the molecules become separated into 2H and 2I. It is easy to understand in this way why there are definite limits of temperature within which chemical changes take place; and how some reactions which occur very rapidly at one temperature may be prevented by suffi-ciently cooling the reacting bodies.

Although as a general rule the action of heat is such as to induce chemical combination at moderately low temperatures and decomposition at higher temperatures, instances are known of bodies being more stable, under certain condi-tions, at high, than at low temperatures. Troost and Hautefeuille (*C. R.* 73, 443; 84, 946) have shown that by passing $SiCl_4$ over strongly heated silicon the latter is volatilised and is again con-densed on the cooler parts of the tube. This apparent volatilisation of silicon was found to be brought about by the formation of Si_2Cl_6 at the higher temperature, and decomposition of this compound into the original bodies at a lower temperature ($2Si_2Cl_6 = 3SiCl_4 + Si$). The com-paratively complex body Si_2Cl_6 is thus resolved by diminishing the temperature into the com-paratively simpler bodies $SiCl_4$ and Si.

A somewhat analogous reaction is asserted to occur by Ditte with SeH_2 (*C. R.* 74, 980). This chemist says that if selenion is heated with hy-drogen in a closed vessel, the amount of SeH_2 formed increases with increase of temperature up to 520°, but that any further increase in the temperature is accompanied by a decrease in the amount of SeH_2 formed. If two tubes are heated under like circumstances until the amount of SeH_2 formed is constant, and one of them is then cooled rapidly while the other is allowed to return gradually to the lower temperature, Ditte says that the second tube contains less SeH_2 than the first, and so much less as the cooling has been slower. On the other hand, SeH_2 submitted to the action of heat suffers sensible decomposi-tion even at 150°; above 270° the amount of de-composition gradually decreases until it reaches a minimum at 520°, after which the decomposition continuously increases as temperature rises.

Chemical systems which are limited by reason of inverse actions may be represented in terms of their rates by the equations $\frac{dv_1}{dt} = f(\theta)\psi(\text{AB})$, and $\frac{dv}{dt} = f'(\theta)\psi(\text{CD})$, in which the accelerating influ-ence of temperature is expressed by the functions $f(\theta)$ and $f'(\theta)$, and the absolute rate by the differ-ence, or $\frac{dv}{dt} = f(\theta)\psi(\text{AB}) - f'(\theta)\psi(\text{CD})$. When equi-librium is attained, or no further change takes place, $f(\theta)\psi(\text{A}'\text{B}') - f'(\theta)\psi(\text{C}'\text{D}') = 0$; A′, B′, C′, D′, being the quantities of active substances that can exist together in stable equilibrium at tempera-ture $\theta°$. If the temperature functions be the same in both cases, then $f(\theta)\{\psi(\text{A}'\text{B}') - \psi(\text{C}'\text{D}')\} = 0$, or $\psi(\text{A}'\text{B}') = \psi(\text{C}'\text{D}')$, or the limits are independent of temperature. This would seem to be true between certain limits for the simpler etherifica-tion processes, as Berthelot and Saint-Gilles' experiments have shown. Menschutkin, how-ever, has examined certain limited reactions which show a marked variation in the limits with temperature, and seem to indicate that the ratio of $f(\theta)$ to $f'(\theta)$ is not constant.

From a study of certain reactions which are not affected by limiting conditions, and of other reactions which are so limited, attempts have been made to determine the accelerating action of heat, that is to say, to determine the form of the temperature-function $f(\theta)$ in the equation $\frac{dy}{dt} = f(\theta)\psi(\text{T}.a.b.c....)$.

Hood (*P. M.* [5] 6, 371), from experiments on the rate of oxidation of ferrous sulphate solution by $KClO_3$, considered that $f(\theta) \propto \theta^2$, or that the rate of oxidation varied as the second power of the temperature; but the experiments were not sufficiently numerous to place this conclusion beyond doubt.

Warder (*Am.* [3] 203) studied the influence of heat on the rate of the action

$C_2H_5O.C_2H_3O + NaHO = NaC_2H_3O_2 + C_2H_5HO$,

in dilute aqueous solutions, the temperature limits being 3·6° and 37·7°. The results obtained agreed well with the formula $(7{\cdot}5 + a)(62{\cdot}5° - t) = 521{\cdot}4$; t being temperature, and a the number of gram-equivalents per litre which would (accord-

ing to the theory of mass) react upon each other per minute in a solution kept of normal strength. The formula could be written as $a = \text{A} + \text{B}t^2$, indicating the rate to vary nearly as the square of the temperature. Menschutkin (*J. pr.* [2] 29, 437) employed three somewhat analogous reactions for the study of this subject: (1) formation of ethylic acetate from acetic acid and ethylic alcohol, (2) formation of acetanilide from acetic acid and aniline, (3) formation of acetamide from acetic acid and ammonia. Molecular quantities of the materials were heated for one hour at different temperatures, and the amounts of ether, anilide, and acetamide formed were determined, and taken as measures of the speeds. The following are his results: —

Temp.	Ether formed	Temp.	Anilide formed	Temp.	Acetamide formed
90°	7·50	82°	6·08	100°	0
102	13·50	92	8·50	110	1·27
112	19·02	102	14·59	121	4·41
122	24·78	112	21·51	130	9·02
132	32·60	122	30·71	140	21·36
142	40·65	132	39·91	150	36·96
152	46·82	142	47·65	152	40·66
162	52·99	152	55·49	155	50·90
172	57·45	162	61·57	160	58·67
182·5	60·99	171	66·39	172	72·33
212·5	63·98	182·5	68·87	182·5	78·31
		212·5	72·19	212·5	82·83

These numbers all agree in this respect, that the differences in the amounts of action during one hour, for equal differences of temperature, gradually increase, pass through a maximum at a definite temperature, and then decrease. As regards the general inferences that might be drawn from these experiments relative to the connection between action of heat and rate of change, it must be remembered that the reactions labour under the disadvantage of being cases of only limited action, and that the products of the change no doubt retard the principal reaction, and tend to complicate matters. Besides this, the method of allowing the change to proceed in each case for the same interval of time is objectionable, for at the higher temperatures the amounts of the products formed before the expiration of one hour are so very much greater than the amounts formed at the lower temperature that their presence must exercise a considerable retarding influence on the further progress of the reaction up to the time-limit.

Unlike some of the etherification processes the limits of formation of acetanilide and acetamide are influenced very considerably by heat, as the following numbers show:—

Acetanilide Temp.	Acetanilide Limit	Acetamide Temp.	Acetamide Limit
100°	80·05	125°	75·10
125	83·11	140	78·18
135	82·39	155	81·46
145	81·22	182·5	82·82
155	79·68	212·5	84·04
182·5	78·85		
212·5	77·75		

In order to determine the temperature function influencing the rate of a chemical change, Hood (*P. M.* [5] 20, 323) has again studied the oxidation of ferrous sulphate solution by potassic chlorate. This reaction is well adapted for work of the kind, as it is completely under control, and can be rendered as quick or as slow as may be desired by altering such conditions as dilution, temperature, amount of free acid, &c. The progress of the oxidation can also be followed with the greatest precision by means of permanganate.

Each experimental solution consisted of ·5637 gram of iron as ferrous sulphate, and 3·099 grams of free H_2SO_4, made up to a volume of 250 c.c. To this solution 10 c.c. of a solution of $KClO_3$ were added, equal to ·2057 gram—being the oxidising equivalent of the iron. From each such a solution, maintained at a constant temperature, 10 c.c. were withdrawn at indefinite intervals of time, and titrated by permanganate, and from several such observations the constants in the equation $y(a + t) = b$ were calculated; y being c.c. of permanganate, and t being time in minutes.

Since b is inversely proportional to the rate of change, or $\frac{dy}{dt} = -\frac{y^2}{b} = -kf(\theta)y^2$, by comparing the values of b obtained from a series of experiments in which everything remains the same except the temperature, a measure is obtained of the influence of heat on the rate of the oxidation, and consequently a means of finding the probable nature of the temperature-function $f(\theta)$.

The following table contains the results of Hood's experiments; the values for a and b for the equation $y(a + t) = b$ being the means of several experiments:—

Temp. C.	t	b	Ratio $\frac{b_n}{b_{n+1}}$
10°	330·8	3327·8	......
11	301·6	3025	1·100
12	274·7	2752·9	1·098
13	250	2503	1·099
14	227·5	2282·7	1·096
15	206·6	2055·7	1·110
16	194·3	1920·8	1·070
17	174·2	1733	1·109
18	159	1577·4	1·098
19	147·1	1452·6	1·086
20	134·4	1325·4	1·096
21	124	1216·8	1·089
22	114·9	1123	1·083
23	102·6	1002·3	1·120
24	94·8	924·5	1·084
25	89·9	869	1·064
28	68·5	654·8	1·099
30	58·7	551·2	1·090
32	50·3	465·3	1·088
		Mean......	1·093

From the numbers under $\frac{b_n}{b_{n+1}}$ it appears that this ratio has as nearly as possible a constant value, the mean of all the experiments being 1·093: it would seem, therefore, that for this reaction at least the temperature-function has an exponential form, and that the rate of

change may be written $\frac{dy}{dt} = -\mu a^{\theta} y^{2}$, θ being the temperature. Calculating the rates of oxidation on this assumption, or $\rho = \mu(1\cdot093)^{\theta}$, where ρ is rate and θ temperature, and comparing them with the rates found by experiment from the values of b, or $\frac{b_{10}}{b_{\theta}}$ the rate at 10°C. being taken as unity, the following numbers are obtained:—

Temp. C.	Rate of oxidation	Calculated rate of oxidation
10°	1·00	......
11	1·10	1·09
12	1·21	1·19
13	1·33	1·31
14	1·46	1·43
15	1·62	1·56
16	1·73	1·70
17	1·92	1·86
18	2·11	2·04
19	2·29	2·23
20	2·51	2·43
21	2·73	2·66
22	2·96	2·91
23	3·32	3·18
24	3·59	3·47
25	3·83	3·80
28	5·08	4·96
30	6·04	5·92
32	7·15	7·07

Investigations of many reactions must be made before it can be determined how far it may be true in general that the rate of a chemical change increases in geometrical progression as the temperature varies arithmetically. Lemoine (*Études sur les Équilibres chimiques*, 178) has expressed the opinion that the temperature-function is of an exponential form; and this he considers to be correlative with the nature of the internal movements which constitute the temperature of a body.

Influence of Light.—A survey of the principal facts that are known relating to the influence of light on chemical changes, or in producing such changes, would seem to indicate the possibility of classifying these chemical changes into (1) such as are only induced by the action of light, or light and heat combined, and (2) reactions which, taking place under ordinary conditions in darkness, are accelerated by the action of light. To the first class of actions belong *par excellence* the photographic processes (of which unfortunately so little is known), and such reactions as the combination of H with Cl, the dissociation of HI, or the reduction of ferric oxalate solution. From the experiments of Amato it would seem that some of these typical changes produced by light can only take place above a certain limit of temperature, indicating that heat as well as light is necessary. To the second class probably a great many, if not all, of the chemical changes that have been studied with reference to their rates, limits, &c., will be found to belong when they have been examined in this respect. but as yet little or nothing has been done. As an instance of the latter class of reactions may be cited the oxidation of oxalic acid by potassic permanganate. Harcourt and Esson (*T.* 156, 194) observed that the rate of this oxidation (which under ordinary conditions is moderately quick) is greatly accelerated in direct sunlight; the amount of this acceleration was not, however, determined.

Hydriodic acid exposed to sunlight for one month at ordinary temperatures is decomposed to the extent of 80 p.c.; but when this gas is heated night and day for the same length of time at 265° in a dark chamber, scarcely 2 p.c. of the hydrogen is liberated.

The analogy between the chemical effects of light and heat is very striking: both agencies act in such a way as to break down or simplify chemical structures, as well as to build up complex molecules from simpler constituents. Many instances might be cited to exemplify these statements; such as the disruption of HI into free iodine and hydrogen, the formation of HCl and of $COCl_2$ by light; and the formation, and at a higher temperature the dissociation, of HI, H_2Se, H_2O, and numberless other bodies, by heat.

There seems, however, to be one marked difference in the modes of action of heat and light. Whereas, in those chemical changes produced by heat which are termed dissociations or disruptions of molecular structures, a limit is reached depending upon the pressure and temperature to which the system is subjected, in similar changes produced by light there seems to be no limit, but the process goes on until complete decomposition is attained. This is easily understood when it is remembered that in such reactions, under suitable conditions, heat tends to destroy as well as to re-form the molecular structures; but that when light acts in such a way as to break down complex molecules the inverse action has not yet been observed to occur under any conditions. For example free H and I exposed for one month to sunlight suffer no measurable change; but HI in the same interval of time is decomposed to the extent of 80 p.c. Reactions of a limited, and perhaps reversible, character, induced by light, analogous with the dissociation phenomena produced by heat, may yet be discovered. Light rays of different refrangibilities induce chemical changes with greatly different intensities, and probably with different effects. Lemoine (*C. R.* 93, 514) has shown that HI is decomposed with facility in vessels made of blue glass, but is very slowly changed in red glass vessels. For those bodies which heat alone decomposes at low temperatures, the extreme red of the spectrum appears much less efficacious than the extreme violet. In the cases of bodies which are stable at high temperatures, if the time of action be long enough, the red rays ultimately produce the same result as the violet. Chastaing (*A. Ch.* [5] 11, 145) concludes that it is not necessary that white light should act more energetically in a given way than any particular part of the solar spectrum, for it is possible that some rays produce the inverse action of others. The chemical action of the solar spectrum on binary metalloid and metallic compounds ought, he thinks, to be represented by two curves, one reducing on the side of the violet, the other of an oxidising character on the red side of the spectrum, and,

he says, there probably exists a point where photochemical action is nil or equal to that which takes place in darkness

An elaborate study of the influence of light in producing chemical changes was made by Bunsen and Roscoe in 1857; some of the facts which their investigations brought out are of a highly important character. Draper in 1843 had observed that the action of light on a mixture of H and Cl does not begin to show itself instantaneously, and he concluded that the first action of light was to bring about a change in the Cl, probably producing an allotropic modification, before combination could take place between it and hydrogen. Bunsen and Roscoe made this observation by Draper the subject of many experiments and measurements. They considered that whatever may be the cause of the resistance to combination which the gaseous mixture shows for some little time after submitting it to the action of a constant source of light, Draper's assumption is not borne out by facts.

The following measurements exemplify this resistance effect as obtained by these chemists with a constant source of light (*T.* 147, 363):—

Time in mins.	Observation	Action during 1 min.
0	100	
1	100·5	·5
2	102·1	1·6
3	102·6	·5
4	103·2	·6
5	105·3	2·1
6	119·9	14·6
7	139·1	19·2
8	170·2	31·1
9	200·6	30·4

These numbers show that about 8 mins. exposure is required before the rate of combination reaches a constant maximum. It was found that the time that elapses, from the first insolation until the first trace of photochemical induction becomes visible, and until the maximum action is attained, varies much according to the experimental conditions. It was also found that the resistance to combination, once overcome by the influence of light, is soon restored when the gaseous mixture is allowed to stand in darkness, but that the increase of the induction from exposure to light takes place much more rapidly than the diminution of the same on darkening. The presence of a foreign gas, or of excess of Cl or H, influences the induction-effect in a remarkable manner. Thus the maximum of the induction of a normal mixture was reduced from 100 to 37·8 by the presence of $\frac{3}{1000}$ of hydrogen, and in the presence of $\frac{5}{1000}$ and $\frac{13}{1000}$ of oxygen it diminished from 100 to 9·7 and 2·7 respectively, and for $\frac{10}{1000}$ of Cl from 100 to 60·2. By insolating the gases separately no appreciable effect was produced on the induction effect when the gases were afterwards mixed.

It is interesting to note that if this preliminary resistance to undergo change is a universal law in such actions as are brought about by light in bodies in the liquid or solid state, it would evidently place a limit to so-called instantaneous photography.

Marchand (*A. Ch.* [4] 30, 302) has studied the influence of light on a mixture of oxalic acid and ferric chloride in aqueous solution. Such a solution placed in darkness suffers no change, but when exposed to light it evolves CO_2 with the reduction of the ferric chloride. Heat alone has no visible effect on the mixture even at a boiling temperature, but if the solution is exposed to solar radiations and is then heated, decomposition takes place with explosive violence. Of the different parts of the spectrum, the blue rays exercise the most energetic action, even more so than the violet rays. Some highly interesting facts have been noticed by Lemoine (*C. R.* 97, 1208), bearing on the chemical changes produced by light with the above mixture. He employed a number of thin vertical glass tubes, 15 mm. diameter, each containing 20 c.c. of a mixture of ferric chloride and oxalic acid; the solutions were saturated with CO_2, and contained equivalent quantities of the reacting bodies. The evolved gas was collected over glycerine. The speed of the reaction increased in proportion to the intensity of the light, but for equal intensities of light the speed was at first approximately constant, and only began to slacken when the liquid had disengaged half the possible quantity of gas. If the two reagents are exposed separately to strong sunlight and are then mixed, the decomposition goes on much more rapidly than if the mixture is exposed to light before separate insolation. The following numbers illustrate this fact; the measurements, which were made after the same intervals of exposure, show an acceleration of about ten p.c. in the latter case:—

	Gas disengaged.							
Liquids not insolated	0	24	52	64	83	93	100	107
Liquids insolated for nine hours . . .	0	24	58	70	91	103	110	117
Ratios . .		1	1·11	1·09	1·10	1·11	1·10	1·09

A remarkable point noticed in these experiments was that the addition of water increased the rate of action of the light. This anomalous effect may have been due to the partial decomposition of the ferric salt, as well as to the fact that the upper layers of the ferric chloride absorb much of the light and prevent it penetrating far into the liquid.

According to Amato (*G.* 14, 57), many reactions which are produced by sunlight are not really due to this agency. Amato considers that light only acts under certain determinate conditions of temperature, and that consequently there are limits of temperature within which light does not act in a chemical way. He found that a mixture of Cl and H, if cooled to −12° could be exposed to the direct rays of the sun for hours without combination taking place. In this experiment care must be taken that the Cl is not exposed to the sun's rays before cooling, as insolation renders chlorine capable of combining with hydrogen even in the dark.

Influence of Pressure.—Many substances when subjected to the influence of heat in a closed vessel, such for instance as calcic carbonate, ammonic carbamate, or paracyanogen, are decomposed or changed to an extent which is found to be limited, for a constant temperature, by the pressure of the resulting gaseous

products.' When the pressure of the evolved gases has reached a definite value no further alteration takes place. If, however, the pressure is maintained below this limit, by allowing the gases to escape, complete decomposition results. The consideration of the influence of gaseous pressure in such instances belongs to dissociation (*q. v.*). There are, however, a few chemical changes known, other than those of dissociation, which occur only under considerable pressures, and others again which are prevented, or at least greatly retarded, by pressure.

Cailletet (*C. R.* 68, 395) found that, representing the amount of action between zinc and HClAq of a definite strength under ordinary atmospheric pressure by 10, the action was reduced to 4·7 under a pressure of 60 atmospheres, and under 120 atmospheres the amount of action in the same time was only ·1. The amount of action between HNO_3 and $CaCO_3$ under pressures of 1 and 150 atmospheres he found to be as 11·09 : 1.

Beketoff (*C. R.* 48, 442) reduced solutions of silver nitrate and sulphate, and ammoniacal silver chloride, by hydrogen, under pressure—reactions which do not take place at atmospheric pressure.

By mere mechanical pressure Spring (*B.* 17, 1218) caused several of the metals, such as copper and lead, to combine with sulphur, and also brought about the formation of many alloys.

CONTACT-ACTIONS.—*Catalysis. Cyclical Actions.*—Catalysis, or contact-action, is the name given to a numerous class of chemical changes that are induced in certain chemical systems by a substance which does not itself undergo any permanent alteration, but which by its mere presence under suitable conditions brings about a re-arrangement among the molecules of the bodies with which it is placed in contact. The material which acts in this manner, without apparently being affected itself by the changes it induces, has been termed a catalytic or contact-agent.

According to the theory of Berzelius, who was the first to study this class of reactions, such bodies are possessed of a peculiar property or power which he termed 'catalytic force,' or the power to bring about chemical changes. Berzelius assumed this catalytic force to be of the character of an electrical force. It seems simpler, however, to regard such actions as being merely manifestations of the same property or power that is exhibited by all forms of matter undergoing chemical change, or the manifestation of the affinities of one kind of matter for another. It is reasonable to suppose that in every chemical system there is a tendency to undergo change of some definite character, such for instance as hydrogen and oxygen to unite, cane sugar and water to form glucose, potassic chlorate to give off oxygen, &c. The conditions under which the system exists may be such that the affinities are in a state of stable equilibrium among themselves. Every system may be regarded as having a weak point, or point of least resistance, at which an alteration will most easily take place. For instance, in the reduction of certain metallic oxides, the oxides are first reduced to lower oxides and then to the metal; or, certain salts are decomposed when heated, but one phase of the change takes place at a lower temperature, or more easily, than another phase. It would seem probable, therefore, that if a suitable material were introduced into a chemical system, it might so react with certain constituents of the system as to upset the previous equilibrium to such an extent that what was before merely a tendency to undergo change would become an actual change, beginning at the point which before the introduction of the catalytic agent was the weakest point of the system. The catalytic agent may be regarded as tending to form, with one of the constituents of the system, a compound too unstable to exist under the conditions, which compound immediately breaks up, leaving the so-called catalytic agent in its original condition, free to react with a fresh portion of the system.

Contact-action would seem to be rather an ill-chosen term for this class of reactions, since all chemical combinations imply contact. It is also well known that many soluble salts if placed in contact with insoluble salts or pps. adhere tenaciously to these. A striking instance of this kind of contact-action is exhibited by metastannic acid. If a small quantity of this powder be shaken up with a highly ferruginous solution of aluminium sulphate, the ferric oxide in solution is seized upon by the insoluble metastannic acid, leaving a solution of aluminium sulphate in which scarcely a trace of iron can be detected.

From the evidence that exists relating to what is strictly known as catalytic action, if a word were necessary to distinguish this kind of change from ordinary chemical reactions, *cyclical action* or *cyclical change* would seem to be near the mark.

The instances that are known among gases in which the presence of a body brings about chemical action in an otherwise stable gaseous mixture seem to be explained by assuming that contact action merely causes a condensation of the gases upon the surface of the material that brings about their union. Faraday (*T.* 1834. 55) found that if a plate of perfectly clean platinum is brought into a mixture of hydrogen and oxygen, combination of the gases begins to take place, at first slowly, but at a gradually increasing rate, until combination occurs with explosive violence. This combination was considered by Faraday to be due to the condensation of the gases upon the metallic surface, whereby the molecules of oxygen and hydrogen were brought into such close contact that chemical union took place. The presence of small quantities of CO or CS_2 prevents the combination of the oxygen and hydrogen by aid of a platinum surface, although the metal is not found to lose its power if afterwards plunged into a pure mixture of the gases. Small quantities of such gases as H_2S or HCl, however, so alter the platinum-surface that the metal is now incapable of effecting the combination of H with O. Other substances, such as charcoal, pumice, rock crystal, &c., act in a similar manner to, but less rapidly than, platinum. Platinum also brings about the combination of SO_2 and O to form SO_3, of NH_3 and O to form HNO_3 and H_2O, &c.

Konowalow (*B.* 17, 1360; 18, 2808), when determining the vapour density of tertiary amylacetate, found that the dissociation-phenomena exhibited by the vapour of this body are influenced in a striking manner by the presence of many finely divided substances such as silica, magnesia, calcium sulphate, &c. The effects varied with the chemical, as well as with the physical, characters of the substances placed in contact with the vapour. To such a slight extent have these contact actions been studied that it seems as yet impossible to interpret them in the same way as those chemical actions which are here termed cyclical. Faraday's theory for the action of platinum in bringing about the union of oxygen and hydrogen by a mere condensation of the gases would seem to be the most reasonable explanation in the face of the facts at present known.

Examples of catalytic actions are known among liquids, which may be explained on the theory of cyclical change; such are the evolution of oxygen from a solution of a hypochlorite when warmed with cobaltous or manganic oxide, and the decomposition of hydrogen peroxide by manganese dioxide, finely divided platinum or silver, or by oxide of silver. The last case is remarkable, for here oxygen is evolved both from the silver oxide and from the hydrogen peroxide; to explain this, and a number of analogous reactions, Brodie (*T.* 140, 759) assumed that atoms of the same body may have an attraction for each other or be in a state of polarisation. Brodie expressed the reaction of Ag_2O with H_2O_2 thus, $H_2\overset{+}{O}\overset{-}{O} + Ag_2\overset{-}{O} = H_2O + \overset{-}{O}\overset{+}{O} + Ag_2$.

The change of cane sugar and water into glucose, and of ethereal salts and water into acids and alcohols, in the presence of acids which themselves remain unchanged, are other instances of catalytic action probably of a cyclical character (see AFFINITY, pp. 71 *et seq.*).

If potassic chlorate is heated alone it melts at about 345°C. and on increasing the temperature to about 370°C. oxygen begins to be produced. Many substances in a fine state of division when mixed with this salt cause an evolution of oxygen much below the temperature at which the chlorate decomposes when heated alone, and without the salt entering into a state of fusion. The substances which facilitate this decomposition do not themselves appear to undergo any chemical change. It is probable that the theory propounded by Mercer (*B. A.* 1842, 32) to explain analogous chemical changes is the true one, viz. that the material which facilitates the decomposition has a tendency to pass into a higher state of oxidation, and that an unstable compound is formed but is decomposed at the temperature of the experiment. On this hypothesis the potassium chlorate is regarded as being decomposed at the lower temperature by the double effect of heat and the affinity of the contact substance—as MnO_2—for the oxygen of the chlorate. Heated by itself, potassium chlorate passes through an intermediate stage in its decomposition with the formation of perchlorate; this intermediate stage is represented according to some chemists by the equation $2KClO_3 = KClO_4 + KCl + O_2$, but it appears to be more correctly expressed by the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$ (Teed, *C. N.* 52, 248). If, however, manganese dioxide is heated with the chlorate, no perchlorate is formed; this fact may be explained and used as an argument in favour of Mercer's view, by supposing that $KClO_3$ when decomposed by itself forms KCl and O_3, and that the nascent ozone oxidises a second molecule of chlorate to perchlorate, whereas in the presence of MnO_2 a higher but very unstable oxide of manganese is formed, and is almost simultaneously decomposed. The oxides which most markedly facilitate the decomposition of potassium chlorate are as a rule those the metals of which form several oxides. It is a well-known fact that the oxygen prepared from $KClO_3$, either by heating the salt alone or mixed with MnO_2, liberates iodine from an alkaline iodide; this is usually considered to be due to a trace of free chlorine; it may, however, be occasioned by a little ozone that escapes decomposition by the MnO_2 or the $KClO_3$.

Contact chemical action, whatever be its true cause, plays a highly important part in several industrial operations, as the inversion of cane sugar, the conversion of starchy matters into glucose, the decolorisation of sugar solutions by charcoal, and probably in the purification of waters by filtration through porous media. Formerly the great industrial processes of fermentation in the formation of alcoholic liquors were referred to this cause, but it seems now certain that such changes are phenomena connected with organic life and not with those of unorganised matter.

(For a theoretical consideration of catalysis see Mendeléeff, *B.* 19, 456.)

A consideration of the facts that are known relating to chemical change shows that in the study of the subject not only must the kind or quality, and the mass, of the reacting matter, be taken into account, but attention must also be given to the intrinsic forces that come into play, as well as to the motion of molecular or atomic motions. It is not at present so much the relative values of these forces that one desires to know, in whatever way they may be measured, as the circumstances under which the forces act, or are modified in their action. It has been seen that all atomic structures are possessed of relative degrees of stability, as is shown when submitted to the action of physical agencies, or when they play an active part in chemical systems, this stability being due to the interaction of the affinities holding the structure together. These forces or affinities offer different degrees of resistance to the action of different agencies, and it would seem to be only by the study of such influences that a rational conception of the nature of chemical action will be arrived at.

That the ultimate constituents of matter—the atoms or molecules—are in continual motion, the interdiffusion of gases, and of salts in solution, seems to prove; and the fact that, in a chemical system undergoing change, such change is more or less gradual, taking fractions of seconds or whole years to be accomplished, seems to offer conclusive proof that the atomic constituents are in a continual motion of interdiffusion. But whether or not the change going on in a chemical system is brought about by simple

collisions among the moving molecules cannot be asserted. For instance, anhydrous alcohol and acetic acid, when mixed in equivalent proportions, react upon each other at ordinary temperatures with extreme slowness; in fact, it takes months to accomplish what at 100° requires only minutes, and yet it is highly probable that very many more collisions occur between the alcohol and the acid molecules than the rate of change would lead us to conclude. It may be that in these and similar cases the molecules of the two constituents of the system must be moving with a definite velocity if chemical action is to occur. But the kinetic theory of gases teaches that in a space of uniform temperature some molecules have high and others low velocities, and that the ratio between the numbers of molecules having high and those having low velocities varies with the temperature; consequently any chemical change which occurs may be but a process of selection among the molecules according to the velocities they possess, those with velocities below a certain limit colliding, but not reacting chemically with, each other.

As chemical reactions are generally formulated, the phenomena of change are for the most part at present viewed only in the light of the distribution of certain masses of matter of various kinds, and no cognisance is taken of the changes in the energies of the systems as these pass from the initial to the final states. In the blank that is at present occupied by the sign '=' lie all the real phenomena of the science of matter. Attempts have been made to fill up this blank by the investigation and measurement of the heat-disturbances that arise when a chemical system passes from the state represented by one side of the equation to that represented by the other side. By virtue of the inherent forces or affinities, as well as by the particular motions of the ultimate particles or atoms of matter, all substances may be looked upon as possessing a certain definite amount of energy, potential as well as kinetical, and consequently as capable of performing a definite amount of work. The tendency of the constituents of a system is invariably towards a state the attainment of which involves a degradation of energy; in other words the total energy of the system tends to fall from a higher to a lower level. (For the general inferences that have been drawn from the study of thermal phenomena bearing on the applications of the laws of energy to chemical change reference must be made to the section on THERMAL PHENOMENA of the article PHYSICAL METHODS USED IN CHEMISTRY.)

It is much to be desired that a classification of the elements, or, what seems more possible, of their compounds, should be attempted, based upon some particular dynamical property which should include not only the conception of mass but also the conceptions of time and work; it is evident, however, that the difficulty lies in the kind of phenomena to be observed and measured. Mills (P. M. [5] 1) has propounded certain ideas relating to chemical phenomena, making motion the basis of the science; and he considers that chemical substances should be valued not for what they are conceived as being, but for what they are capable of doing. Doubtless, however, the being as well as the doing must be considered together. The masses of various bodies necessary for the performance of unit of work Mills terms the dynamic equivalents, or the 'bergmannics,' of the respective bodies; these may vary according to the sort of doing, or work, the several substances are employed to effect; such as the power of various acids to invert sugar, or to decompose ethereal salts, the precipitability of salts, the coefficients of diffusion, &c., &c. For many valuable determinations of dynamical effects of substances in inducing or accelerating chemical changes, see the work of Ostwald. For a full account of this work *v.* the article AFFINITY. (In connexion with this article, *v.* the articles: AFFINITY; ALLOTROPY; CHEMICAL AND PHYSICAL PROPERTIES OF BODIES, CONNEXIONS BETWEEN; COMBINATION, CHEMICAL; DISSOCIATION; EQUILIBRIUM, CHEMICAL; ISOMERISM.)

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END OF THE FIRST VOLUME

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